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THE

METALLOGRAPHIST

A Quarterly Publication devoted to the Study of Metals, with

Special Reference to their Physics and Microstructure,

their Industrial Treatment and Applications.

Edited by ALBERT SAUVEUR.

VOL. I.

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CONTENTS.

* Frontispiece, Fig. 2, should read "Magnified 500 diameters."

FIG. 8. Steel — 1 per cent Carbon.
Forged and reheated to 800° C.   Polished in relief.
Magnified 1000 diameters.
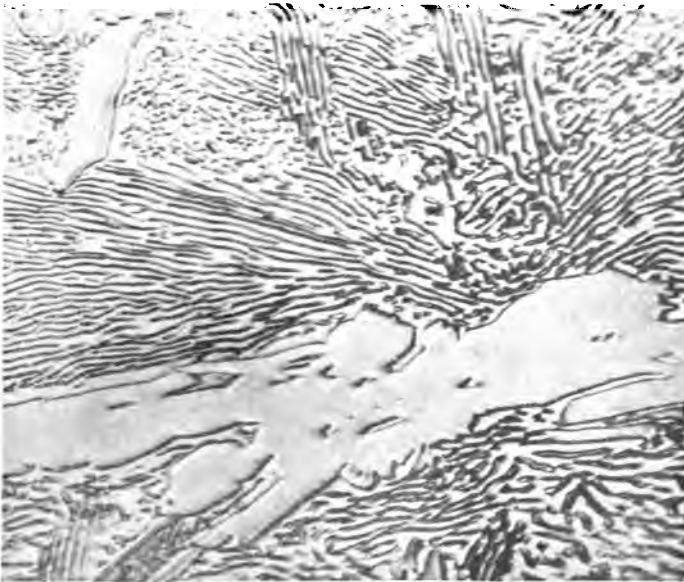
FIG. 9.   Cemented Steel — 1.5 per cent Carbon.
Untreated.   Combined polishing and etching.   Magnified 1000 diameters.

PHOTOMICROGRAPHS OF STEEL, after OSMOND.

INTRODUCTORY.

THE PURPOSE OF "THE METALLOGRAPHIST."

I F it were asked what product of the physical universe has
most contributed to the industrial progress of the world,
to the material comfort of the human race, it could be con-
fidently asserted that metals are entitled to the first place.
Indeed, should the metals be removed from our present social
and industrial organization, the whole structure would igno-
miniously collapse. For can we conceive of a civilization
without dynamos or steam-engines, without telegraphs or
railroads, without those invaluable mediums of exchange, gold
and silver; a civilization without metallic tools, and therefore
without the products of tools! One needs reflect but an
instant to realize all that this would imply. Indeed the very
garments we wear would be taken away from us, and we
should be left upon the bare ground where once stood our
beautiful cities, with all the comfort and luxury of a refined
civilization, a testimony of the genius of man, and of the
wonderful adaptability of the products of the earth.

Nor is it only in the material development of the race
that metals have played such an important part, for our
printing presses also are metallic productions, and without

them we would have practically no books, which would mean
the diffusion of knowledge, and therefore our intellectual
growth, tremendously hindered.

The word metal at once suggests strength, solidity,
durability, efficiency, usefulness, trustworthiness.   As pure
as gold, as true as steel are well-earned testimonies. An iron
will stands for a will which does not falter.   Reliableness is
perhaps the quality of metals which should most endear them
to us.   From the knowledge that they will not fail us we
derive a feeling of security, which leads us daily to intrust
our lives to their stanch qualities, be it in our fast-moving
trains, over our frail-looking bridges, in the vicinity of boilers
and fly-wheels, or on the twentieth story of one of our modern
buildings.   And if rails and axles do occasionally break, if
bridges and buildings occasionally collapse, if steam-boilers
explode, if a fly-wheel sometimes goes to pieces, could we
only ascertain, in every case, the cause of the failure, it would
invariably be found that man, not the metal, was at fault. .
We should invariably discover that the failure was due to a
faulty construction, to a defective process of manufacture, or
to some injurious treatment of the finished product.   We
should find that man had violated some law of nature, which,
like all such transgressions, led to the inevitable penalty.
Such instances of failures illustrate only more forcibly their
wonderful efficiency, and the confidence which can be placed
in metallic productions which have been created and erected
in strict accordance with their chemical and physical proper-
ties, and the general laws of nature.

Seeing what metals mean to mankind, what momentous
changes their successive discoveries and uses have brought
into its condition, it is not to be wondered at that ever since
the primeval man discarded his crude stone implements, hav-
ing learned the infinitely greater superiority of those made of
copper or bronze, ever since he succeeded in extracting from
its refractory ore a handful of metallic iron, his descendants
have been incessantly at work in their eagerness to wrench
from the earth the precious metal-bearing product, in their
exertion to increase the purity of the separated metal, and to
perfect its treatment in order to enhance its efficiency and
reliability.

What a struggle, what an amount of energy, of incessant toil, what sweating of the flesh and brain are evolved at the thought of the giant task accomplished by the metallurgist! He may well be proud of its wonderful achievements; he holds a just claim to the everlasting gratitude of mankind. We may look with some complacency upon the achievements of a Bessemer or a Deville, for they are not merely the results of the toil of a human life — generations stand behind them which for centuries have worked at the problems solved by them, until the constituent parts were ready for their masterly touch. They are among the chosen few, intrusted with the spark of genius which gives life and unity to the collective work and thought of mankind.

The efforts to increase the efficiency of metals, to increase their reliability, to make them fulfill new needs, has gone on incessantly, and wonderful results have indeed been obtained — results which would have been considered impossible of realization by the last generation — so remarkable, that to the uninitiated our methods must appear well-nigh perfect.

And yet how far we still are from perfection, that unattainable goal of human ambition. How much is still imperfectly understood in the extraction of metals, and in their subsequent treatments. How many phenomena remain unexplained, how many failures which thorough investigations still leave unaccounted for. The field of researches, the room for improvement, is still wide, and indeed widens and opens up new possibilities as we proceed forward in our eagerness for more knowledge, for a better understanding of the intimate properties of metals.

The last decade has witnessed an activity in metallurgical researches which has probably no parallel in the history of the science, owing to the strictly scientific spirit with which they have been conducted. Scientists in all metallurgical countries have taken hold of the industrial metals, and are applying to them the scientific methods of investigation of this highly scientific age. Witness the work of Sorby, Abel, Müller, Osmond, Howe, Martens, Arnold, Wedding, Roberts-Austen, H. Le Chatelier, Charpy, Ledebur, Behrens, de Benneville, and others.

The metals and their alloys are being dissected, and the

high-power objective, that wonderful instrument of modern
researches, is revealing to us their intimate structure, throw-
ing a flood of light upon their constitution, chemical and
physical, the practical as well as the theoretical value of
which could hardly be overestimated. Their physics, hitherto
much neglected, is being minutely investigated. Their ther-
mal behavior is being ascertained with a precision rendered
possible only by the extremely delicate pyrometer of H. Le
Chatelier. Their magnetic properties, their electric conduc-
tivity, their diffusion, their physical and mechanical properties
in general are being investigated with a degree of accuracy
never before attained. The chemist is energetically at work,
in his endeavor to establish the true chemical relation between
the metals and their impurities, and successful excursions are
being taken in the domain of their proximate compositions.
As Mr. Osmond has aptly said, modern science is treating the
industrial metal like a living organism, and we are led to
study its anatomy, i.e., its physical and chemical constitution;
its biology, i.e., the influence exerted upon its constitution by
the various treatments, thermal and mechanical, to which the
metal is lawfully subjected; and its pathology, i.e., the action
of impurities and defective treatments upon its normal con-
stitution.

Unfortunately, and here we come to one of the purposes
of the present publication, the results of these important
researches are now disseminated throughout the scientific
papers and transactions of scientific societies chiefly of France,
England, Germany and the United States, and even if the
busy engineer or metallurgist, the metal producer or con-
sumer in general, had the necessary knowledge of the three
languages, and easy access to these publications, he could
not possibly find time to go over such an amount of literature
in order to extract from it what is of interest and importance
to him. This is precisely the work which *The Metallographist*
proposes to do for its readers by presenting to them every
three months a clear, exhaustive and comprehensive review
of what has been accomplished in metallography during the
previous quarter.

The most important articles and memoirs will be repro-
duced in full, while those of minor importance will be con-

derised, accompanied in every case by such explanatory notes as will make them comprehensible and fruitful for others besides specialists. *The Metallographist* will publish moreover, besides the results of the investigations·carried on in the Boston Testing Laboratories, original· articles by eminent authorities and active workers who have kindly promised their collaboration. The editor will never lose sight of the fact that the importance of these investigations, to the world at large, lies chiefly in their ability to lead to deductions of industrial value, and his presentation of the subject will be conducted accordingly.

It is believed that there is a need of a publication of this kind in the engineering world, and the editor hopes to conduct it so as to meet with the approbation and encouragement of those interested in metallurgical progress.

If it can contribute a little to the advancement of metallurgy by diffusing a knowledge at present the exclusive possession of a relatively small number of specialists, thus helping metallurgy to approach nearer the sphere of a more exact science, where uncertainty of treatment and uncertainty of results will be gradually eliminated, the editor will feel well repaid for his efforts.

METALLOGRAPHY CONSIDERED AS A TESTING METHOD.*

By F. OSMOND.

Definition. — Metallography, generally speaking, signifies the description of the structure of metals and of their alloys. The science is not confined to the use of a single instrument, the microscope for instance, whose manipulation requires a certain training, giving rise, therefore, to a speciality and to specialists. In reality we begin by using our eyes in the examination of metals, and when they have shown us all that they can see, we provide them with lenses of increasing magnifying power, until we are stopped, at about 2000 diameters, before the mysteries of the ultra-microscopic. But the

* Paper read at the Stockholm Congress (August, 1897) of the International Association for the Testing of Materials, slightly abridged.

naked eye and the optical instruments are only an incomplete
means of investigation.   They take, so to speak, a first
inventory; the indications furnished by the visible characters,
form, color or luster must be controlled by chemical analysis,
micro-chemistry and crystallography, by the determination
of physical and mechanical constants, in a word, by all the
available means for the differentiation and identification of
bodies.

Comparison with Natural Sciences. — To better illustrate the
purpose and the methods of metallography, we can borrow a
comparison from the natural sciences. *Anatomy* recognizes
in the animal body a certain number of organs, the appear-
ance or nature of which, however, cannot be conceived from
their chemical composition as ascertained by ultimate, or
even by proximate analysis.   If the elements or compounds.
thus found in one organ, a bone for instance, were brought
together in the required proportions, they would not evidently
form a bone, or even give us any idea of what a bone is.   We
must call *histology* to our assistance, in order to define the
structural forms and the respective topographical positions
of the bones.   Only then do we come to a precise notion of
that organ.   It still remains, however, an inanimate sub-
stance.   We must now ascertain how the cells, of which we
only have sketched the shape and measured the dimension,
assimilate their nutriment, and eliminate their excreta, in a
word, how they live ; and we are here in presence of a new
science, *biology*.   Finally, the vital processus do not always
follow their normal course; they are disturbed by the intro-
duction of foreign factors, animated or chemical, microbial
or toxic ; the organs may be diseased, and the science of
pathology treats of the causes and effects of those diseases.

The ultimate chemical analysis of an alloy does not tell
how the elements are associated with each other, whether
they form isolated definite compounds, or whether they form
dissolutions, homogeneous or not.   The proximate analysis,
which is not always possible in the present condition of
chemistry, does not tell how the constituents, supposed to be
chemically separated, are organized individually, or how
they are topographically distributed with regard to each
other.   The histological organization and the anatomical

distribution once known, do not tell what modifications the original arrangement will undergo under the influence of certain changes of temperature and of pressure. Finally, these normal modifications, when they also are known, are exposed to great disturbances by the introduction of a minute quantity of some accessory impurity, sometimes inevitable, and whose presence even is not always suspected.

And so we are led to establish several subdivisions in the study of metallography, very analogous to those of medical science, and to talk of anatomical, biological and pathological metallography.

The first subdivision will distinguish the various constituents detected in an alloy by means of their optical (color, luster), their chemical (resistance to re-agents, formation of colored films) or their mechanical characteristics (abrasive resistance, mineralogical hardness); to describe their forms, crystalline or not, to measure their absolute or relative dimensions, to examine their surfaces of weakness (joints or cleavages) which separate them from each other or cut across them.

The second subdivision will ascertain how the composition, the forms, the dimensions and the relations of the various constituents, determined in the static state in a given sample, are related to the possible conditions of the thermal or mechanical treatments to which the alloy may be subjected during the process of its manufacture or during its use.

The third subdivision will consider the influence of defective treatments and of the presence of impurities, and it will often be possible, the effects once connected with their causes, and by proceeding from one to the other, to trace them back for the solution of the problems of daily practice.

It remains to illustrate these three subdivisions by appropriate examples.

Anatomical Metallography.

Substances chemically homogeneous. — Let us take, as a first instance, an elementary substance, cast silver. Its structure is made up of large cubes, themselves composed of smaller secondary cubes symmetrically arranged. It is readily understood that the cleavages of those cubes must constitute natural surfaces of rupture.

If we examine through the microscope a forged sample
of basic steel taken from the open-hearth furnace before the
casting of the metal, and containing 0.12 per cent of carbon and
small quantities of other impurities, being therefore almost
pure iron, we find its structure composed of adjoining poly-
gons, which represent as many sections through polyhedric
grains.

Those grains, strictly speaking, are not crystals, since
they have neither plane faces nor regular geometrical forms.
Yet they are not all identical; the polishing upon parchment
does not wear them at a uniform speed; nitric acid and
iodine do not attack them uniformly. The cause of those
differences is due, at least in part, to the crystalline orienta-
tion of the crystallizing paste, orientation which varies from
one grain to the other, but remains constant in the whole
mass of the same grain. To illustrate that fact, the section
should be etched somewhat deeply with warm dilute sulphuric
acid. The grains which are cut in a direction parallel to two
of their axes exhibit small cubes symmetrically piled up,
very similar to those of silver. If the plane of the section is
parallel to one axis only, the etched grain appears lamellar,
and the structure becomes confuse when the section is not
parallel to any of the grain's axes. We are, therefore, in
presence of two net-works of surfaces of weakness: one due
to the cleavages in the interior of the grains, the other to the
mutual limitation of the adjacent grains of different orienta-
tion. And those surfaces of weakness constitute a natural
receptacle for the gases which may be evolved at the time of
solidification or later, a way all prepared for the fissures
which may be produced or be propagated by mechanical
efforts. The metallurgists must endeavor, if not to suppress
them, which is not possible, at least to attenuate them, by
diminishing the quantity of the gases, in preventing their
evolution, in interfering with the free action of the crystalline
forces by accelerating the cooling, in a word, by all the means
suitable to diminish the extent of the joints' surfaces, and to
make them more disconnected.

It is seen that a substance homogeneous for the chemist,
may be very complex mechanically speaking. But chemic-
ally homogeneous substances are themselves an exception,

and it is generally necessary to differentiate first the chemic-
ally distinct constituents.

Substances chemically heterogeneous. — The simpler case is
that of two constituents of different colors, which makes them
distinguishable by simple inspection of a plane section.
Fig. 1 shows an alloy of 54 per cent of gold and 46 per cent of
aluminium. It contains a component of a beautiful purple
color discovered by Prof. Roberts-Austen; it is a definite
compound answering to the formula $AuAl_2$, which possesses
the very rare property of having a melting-point superior to
the melting-point of the less fusible of the two constituents.

During solidification it separates first as crystallites,
which appear black in the photograph; the interval being
filled by a matter of subsequent solidification, whose propor-
tion and nature vary with the composition of the alloy.

When the constituents have no distinctive color of their
own, which is generally the case with metals, it may be
attempted to color them artificially.

Tincture of iodine, for instance, furnishes a means to
identify lead in many of its mixtures, through the formation
of its yellow iodide. But the precipitates produced in this
way through a chemical reaction do not always adher to the
metal, being easily removed when whipping the preparation;
it may be convenient to fix those colored films upon the
sample, as recommended by Mr. H. Le Chatelier, by means
of a thin leaf of gelatine, soaked with a suitable re-agent,
and applied upon the surface to be examined. The chemical
reaction may also be made to take place while the specimen
is under the microscope.

A second method consists in producing an adhesive film,
too thin to possess a color of its own, but which communicates
to the reflected rays a coloration varying with its thick-
ness. They are the so-called tempering colors. As they do
not appear on the metals which are not oxidable, and do not
appear simultaneously, under similar conditions, upon metals
inequally oxidable, that method is of frequent application.
It is in this way that Prof. Martens obtained the beautiful
photographs of spiegeleisen which illustrate his first publica-
tion, and which are one of the first successes of the then
newly born metallography. That metal is composed of two

constituents : a definite carbide (Fe, Mn)$_3$C and a solution of carbon (or of carbide) forming the balance of the alloy. The definite carbide is relatively little oxidizable, and assumes, after being heated for some time at a certain temperature, a yellow coloration for instance, while the solution has already reached the blue color. The colors thus obtained have the great advantage not to fade under high magnification. Messrs. Wedding, Behrens and Guillemin have used them frequently; and they are of great service in the study of copper alloys.

FIG. 1. Au 54 per cent — Al 46 per cent (cast).
Polished upon a plane surface.
Magnified 100 diameters.
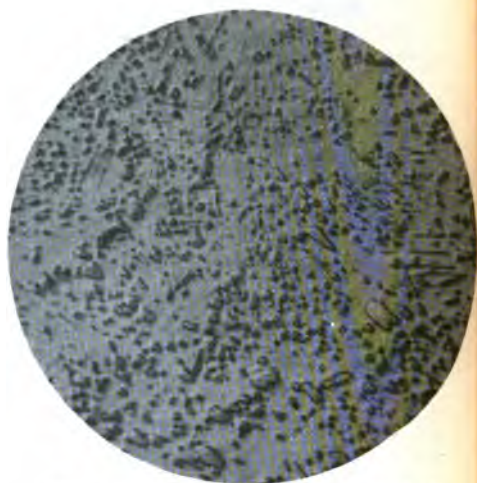
FIG. 2. Forged Steel (1.24 per cent C).
Polished in relief.
Magnified 1000 diameters.

When the constituents are too small to be distinguishable, even under the microscope, the relief effect produced by an etching of varying intensity still gives rise to a decomposition of the reflected light; as the etching deepens, yellow, brown, blue and black colorations appear successively under direct reflected light, but they must not be confounded with the colors produced by heating, for, unlike these, they are not due to the presence of a colored film. This gives a third method of differentiation, which extends somewhat the power of the microscope, but which gives only one indication, merely, that the constituent under examination is not uniformly acted

upon. Colorations, real or artificial, are not the only resource of anatomical metallography. The mechanical properties of bodies may be utilized. Mr. Behrens has prepared a whole series of needles of hardness with which he goes over the surface of the polished section; a certain needle may scratch a certain constituent, and not the other. In the case of bronzes, whose composition is represented by the formula $CuSn_8$ or $CuSn_2$, Mr. Martens has been able, not only to ascertain, but to measure by means of the sclerometer the hardness of each structural element.

The mineralogical hardness of bodies, however, does not depend upon their nature only, but also upon their absolute dimensions: a glass plate sufficiently thin may be, if not scratched, at least cut by the finger-nail, and the result is the same. The method therefore can only be applied to relatively coarse structures. But similar information may be obtained, in the case of more delicate structures, by abrasion upon a soft foundation with the assistance of very fine powders. Fig. 2 shows the structure of a sample of hard steel (1.24 per cent of carbon), forged into a round bar, 12 mm. in diameter, the forging having been ended at a dark red. A cross-section was polished, and the polishing continued upon a piece of wet parchment covered with a very small quantity of rouge; the iron was dug out, placing in relief the carbide Fe_3C which in this sample is divided into a multitude of small rounded grains. The carbide grains appear dark upon a light background, or light upon a dark background, according to the position of the objective: a little above or a little below the focal point. (Fig. 2 was taken in the first of those two positions.) The same result would be obtained by etching the metal with an acid which attacks the iron without dissolving the carbide to any extent; but as the iron, on being thus acted upon, loses its polish in a somewhat irregular way, the preparation often lacks distinctness. Finally, the two methods may be combined by using, instead of water, when polishing upon parchment, an extract of licorice-roots, which, under the influence of prolonged rubbing, slightly dissolves the iron without depriving it of its polish. The method is convenient to resolve clearly that peculiar constituent of slowly cooled steels, whose discovery has brought so much

fame to Dr. Sorby, the founder of microscopic metallography. It is a mixture of iron with the carbide Fe_3C, in alternate layers generally curved (Frontispiece, Figs. 8 and 9); the thickness of a pair of lamellæ does not probably exceed $\frac{1}{1000}$ mm. in an average; it may be much less, and the unequal relief of the two components gives rise, on account of the decomposition of the light, to irisated effects suggestive of those of mother-of-pearl; whence the name of pearlyte, proposed by Mr. Howe with the approbation of Dr. Sorby, and which is adopted to-day by several writers.

Sources of Errors. — The foregoing methods for the distinction of two constituents do not always give conclusive indications. A substance which is chemically homogeneous may offer a resistance to chemical or mechanical action varying much in intensity, according to its crystalline orientation, and according to its degree of compactness. On that account two different appearances of the same constituent may easily be mistaken for two different constituents; and, certainly, confusions of this kind have been made more than once. The skepticism of certain minds, concerning the affirmations of metallographists, has therefore, in principle, some foundation; investigators must test their own methods by multiplying the number of observations, and give only as definitive the concordant results of several independent methods. But that necessary verification has been done in several instances. It has been said, for instance, that the appearance of pearlyte under the microscope did not indicate the existence of two different substances, but only the lamellar structure of a single component, which is more readily and more deeply attacked along the cleavages. The objection, in itself, is reasonable; but those hard plates of carbide of iron which are seen under the microscope have been chemically isolated by Müller, by Abel and Deering, by Osmond and Werth, by Arnold and Read, by Mylius, Förster and Schöne, and it is not possible to-day to contest their independent existence. As, on the other hand, the carbide Fe_3C, isolated by the best methods, represents in the case of slowly cooled steels nearly the totality of the carbon, it cannot be doubted that the second constituent, ferrite, is almost pure iron. Such is no longer the case, however, after rapid cooling, even if the cool-

ing was not sufficiently sudden for hardening purposes. The ferrite, then, would include a certain proportion of the carbon in a chemically distinguishable condition: *hardening* carbon. Thus it is that micrography and chemistry continually assist each other. The former reveals the existence of a mechanical mixture, whose nature the latter seeks to ascertain; or else the analyst separates first certain definite constituents, which the micrographist has then merely to locate.

Biological Metallography.

Generalities. — In the preceding chapter we have seen by what methods the various structures and various constituents may be differentiated. That distinction once made, the determination of the forms and of the dimensions do not present any difficulty, and we are ready to study the biological problems, i.e., to connect the changes of structure with their causes. The transformations, reversible or not, which a metal or an alloy may undergo in the conditions, normal or experimental, of its manufacture or of its use, constitute its life.

The factors of these transformations are, as in the case of living organisms, the temperature and the pressure; and, as their velocity is generally finite, time also must intervene.

The changes which may take place in the structure and in all the properties of a metal, generally, when the temperature varies with a given velocity, are of two kinds: the continuous changes and the critical changes.

The critical changes are those which correspond to a sudden modification in the relation between a certain property and the temperature. Upon the curves which represent that relation they are usually indicated by the intersection of two branches.

These critical changes are evidently the most important to be considered, since they divide the total scale of temperature in as many ranges during which the substance under examination undergoes only slow and progressive, and therefore easily controllable modifications. It is known, moreover, that these critical changes are caused by a sudden change of energy, which indeed reveals them.

The knowledge of these sudden changes of energy con-
stitutes therefore a first information of capital importance in
the study of bodies.

Every metal possesses at least two such changes: its
melting-point and its point of volatilization. These are the
changes of state. Certain substances, much more numerous
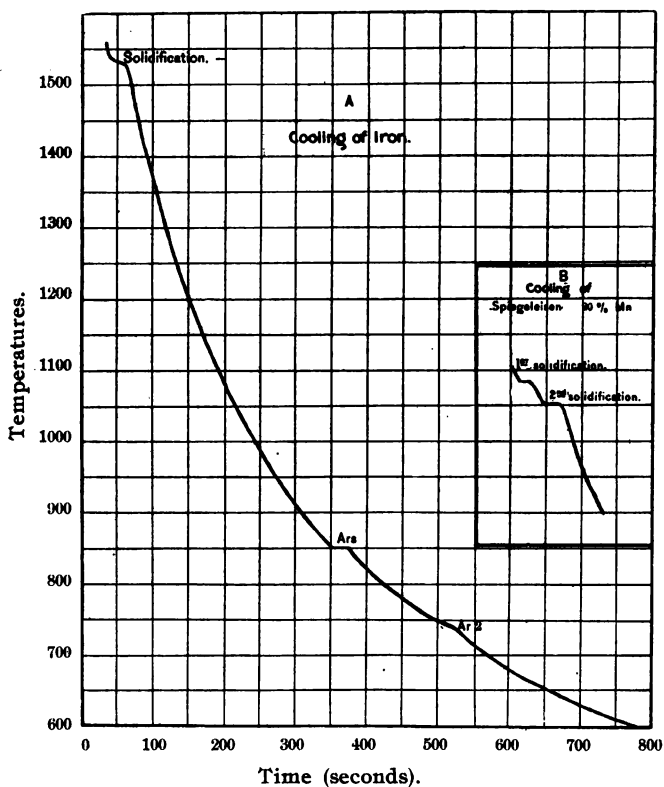
FIGS. A. AND B.

probably than is generally believed, have other points of
transformation which are called allotropic or isomeric changes:
the former in the case of elementary bodies (iron, nickel,
cobalt, sulphur, etc.), the latter in the case of compound
bodies (iodide of silver, nitrate of potassium, etc.).

Iron. — If, for instance, pure iron is allowed to cool
slowly from above its melting-point, and the temperatures

platted in function of the time, the curve will indicate three
stops, or at least three retardations in the rate of cooling.
The first towards 1530° C. corresponds to the solidification,
the second at about 860° and the third between 750° and 700°
correspond to two allotropic transformations; and the whole
curve has the general appearance shown in Fig. A.

Spiegeleisen. — If, instead of elements or of compounds
chemically homogeneous, complex substances are considered
mixtures of several constituents, they will have as a rule as
many points of solidification as they have constituents, to say
nothing of the allotropic or isomeric transformations which
are possible in each constituent. Spiegeleisen with 20 per
cent of manganese has two points of solidification, the first
towards 1085° C., the second at about 1050° (Fig. B.).

Micrography, assisted, if need be, by chemistry, will help
us to interpret those cooling-curves, and to establish the
exact signification of those stops or retardations, often so
mysterious, always so important, which they contain.

Alloys of Silver and Copper. — Let us pass now from an
isolated alloy to the group of binary alloys, which can be
formed by two given metals. Much impulse has recently
been given to such studies by committees placed under the
patronage, in England, of the Institution of Mechanical Engi-
neers, and in France, of the Society of Encouragement. If
the percentages in weight of one of the metals are taken as
abscisses, and those temperatures at which take place, for
each composition, the evolutions of heat during slow cooling
from the melted state, as ordinates, then by connecting the
corresponding points, curves are obtained called curves of
fusibility. The appearance of such curves gives very useful
information regarding the chemico-physical relation of the
two metals. Let us take, for instance, a relatively simple
case, that of alloys of silver with copper. The curve of fusi-
bility of these alloys has been constructed as early as 1875 by
Mr. Roberts-Austen, as accurately as it could be done at that
time, verified in part by the same authority in 1891 by means
of a Le Chatelier pyrometer, and ascertained again in recent
times by Messrs. Heycock and Neville. That curve (Fig. C.)
is therefore perfectly known; it is composed of two inclined
branches starting from the respective melting-points of copper

and of silver, and crossing each other at 770°, for a composition answering to the formula Ag_3Cu_2. A third branch, horizontal, passes by the melting-point, which indicates that copper and silver form neither definite compounds nor isomorphous mixtures. If the present theory of solutions is true, as it has been established by Mr. H. Le Chatelier especially, then one of the branches corresponds to the beginning of the solidification of copper, the other to the beginning of the solidification of silver, and the horizontal branch to the simul-
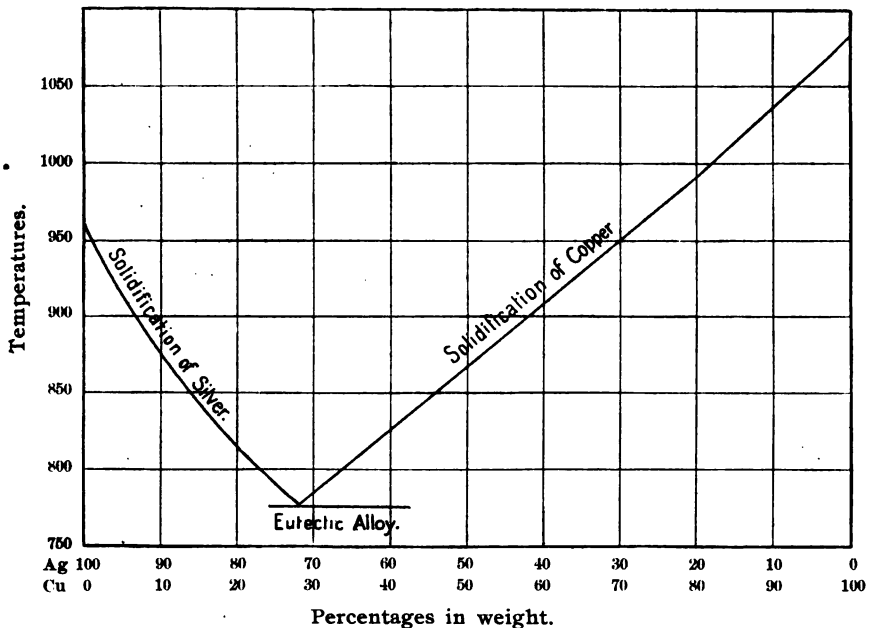
FIG. C. Curves of Fusibility of Ag and Cu Alloys (Heycock and Neville).

taneous solidification of the two metals. In other words, according to the composition of the alloy, the metal which is in excess begins to separate from the dissolution at a certain temperature, and continues to be precipitated until the portion remaining liquid contains 72 per cent of silver and 28 per cent of copper; at that instant the silver is saturated with copper, the copper is saturated with silver, and the two metals solidify simultaneously at a constant temperature, forming a mechanical mixture. It is the alloy called *eutectic*, the only one

which does not segregate in castings, as Leval had shown long ago.
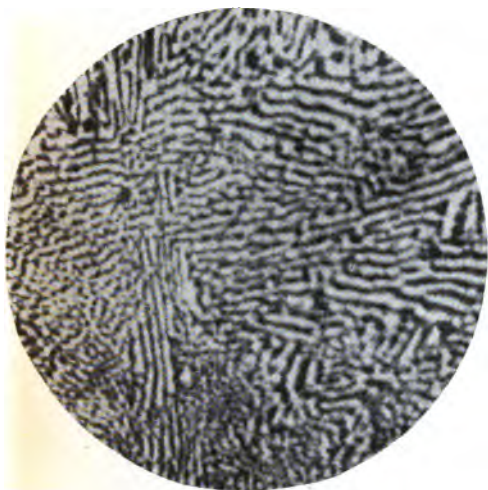
FIG. 3. Cu 28 per cent — Ag 72 per cent (cast).
Reheated to a purple color.
Magnified 1000 diameters.
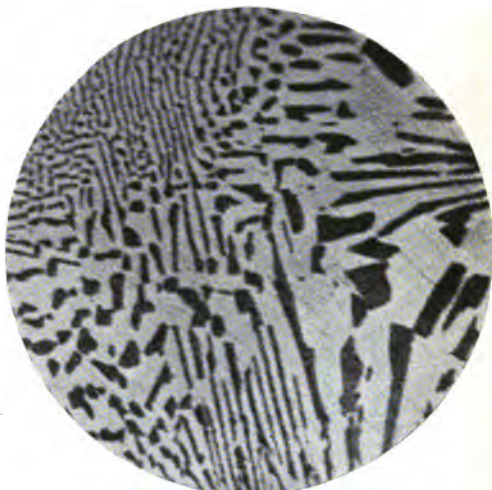
FIG. 4. Cu 28 per cent — Ag 72 per cent (cast).
Reheated to a purple color.
Magnified 600 diameters.

FIG. 5. Cu 15 per cent — Ag 85 per cent (cast).
Reheated to purple color.
Magnified 600 diameters.

FIG. 6. Cu 65 per cent — Ag 35 per cent (cast).
Reheated to purple color.
Magnified 600 diameters.

But as that alloy of Leval, upon being analyzed, indicates a definite atomic formula Ag_3Cu_2, and as its surface exhibits

a very distinct crystallization, scientists were reluctant to remove it from the list of definite compounds, fearing that it might place the theory at fault.

Micrography resolves the question in the simplest and surest way. It suffices for that purpose to prepare a well-polished section upon which· the two component metals may be distinguished by their respective colors. Moreover, by means of a proper reheating, the copper may be made to assume a beautiful orange coloration, while the silver remains white. This shows that the alloy of Leval is by no means homogeneous. Its structure is identical to that of the pearlyte of steel: the yellow metal is distributed either as small dots or as straight or curved plates alternating with the white plates of silver. Those alternations, after a reheating which creates slight differences of relief, give rise to the familiar irisated effects suggested by the word pearlyte. The grains formed first require a magnification of 1000 diameters to be properly resolved (Fig. 3): they are surrounded by a net-work with a coarser but exactly similar structure (Fig. 4). The alloy with 72 per cent of silver is therefore, without doubt, an eutectic alloy, as the fusibility-curve suggested, and the compound Ag_3Cu_2 does not exist.

In other alloys of the same group, crystallites of silver are first deposited if the alloy contains over 72 per cent of silver, while, if it contains less silver, crystallites of copper separate first, in both cases increasing in size until the portion remaining liquid has reached the required composition; the eutectic alloy, then, solidifies at a constant temperature, surrounding the crystallites as shown in Figs. 5 and 6.

Mr. Charpy has studied several similar cases. If the cooling is hastened by casting the alloy in a cold metallic mould, instead of letting it cool in the reheating-furnace itself, the eutectic alloy still exhibits, after reheating to an orange color, a tendency to form plates as shown by the effects of light; but the plates are not distinct, and the general coloration of the preparation remains nearly uniform under the highest magnifications; the metals did not have time to segregate.

In reality, the two constituents of the copper and silver alloys are not made up of pure copper and pure silver, as it

might be inferred from their respective colors. The copper holds a little silver, and the silver a little copper. This can be ascertained in examining alloys which contain one of the metals in small proportions. The latter begins to appear, in distinguishable independent grains, only when more than one per cent is present; and for larger amounts the visible pro-
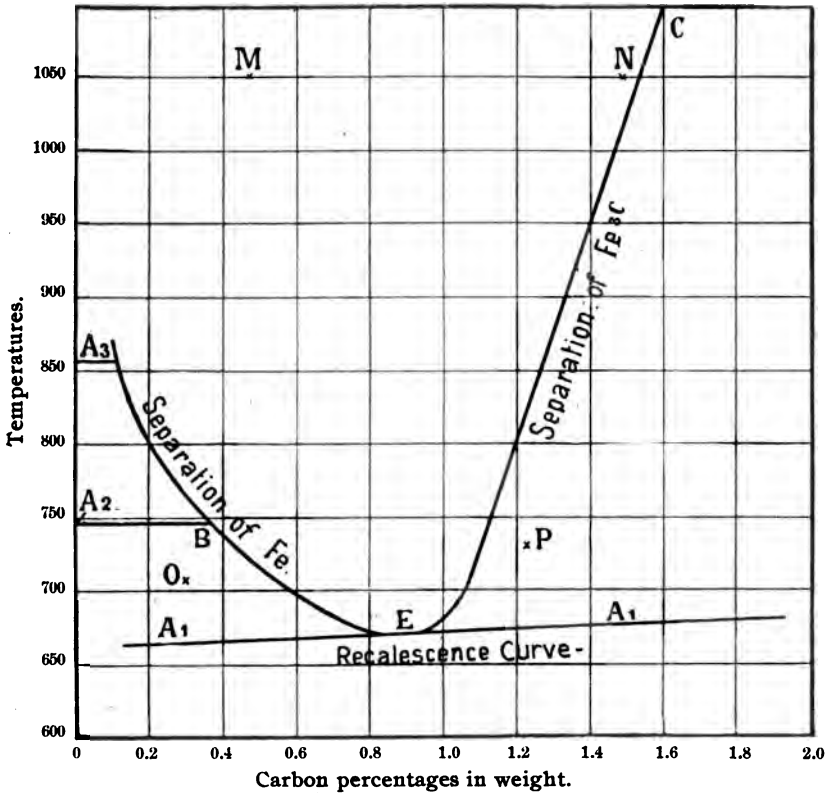
FIG. D.   Transformation Curves of Steels.

portion, estimated from the measurement of the area it occupies, remains inferior to the actual amount added.

Steels. — This leads us to the notion of solid dissolutions, of which we have a very conclusive instance in steels.

Let us take as abscisses the carbon-contents, from o to 1.60 per cent, and as ordinates, the temperatures, as we have already done.

For each carbon-content let us plot on the corresponding ordinate the temperatures at which begin the various evolutions of heat: we obtain in this way a series of curves (Fig. D.).

The branches A_3B and A_2B represent allotropic transformations of the iron, transformations which Bergmann had suspected, more than a century before their discovery, when he said: "Adeo ut jure dici queat polymorphum ferrum plurium simul metallorum vices sustinere." Both branches are united into a single one BE, when the carbon-content exceeds 0.20 per cent and this double branch crosses, at E, another one inclined in the opposite direction, whose meaning will be shown later. Finally, a horizontal line A_1EA_1, passing by the point of intersection, corresponds to the point A of Chernoff: it is the temperature above which steel begins to acquire its hardening power. The passage by the point A is accompanied by a temporary dilatation which breaks the regularity of the shrinkage, and by a sudden evolution of heat, sometimes visible with the naked eye, whence the name of recalescence.

The phenomenon has been studied, from a metallurgical point of view, by the Swedish engineer Brinell, in a series of remarkable investigations in which the author succeeded to replace the instruments which he lacked by a rare observing power. The point E, where the three branches meet, corresponds, according to Arnold, to 0.90 per cent of carbon, or more roughly to an amount of carbon included between 0.80 and 1 per cent.

It will be seen that the diagram taken as a whole recalls exactly the diagram of fusibility of silver and copper alloys. On the other hand, micrographic researches have shown that the branch BE corresponds to a separation of practically pure iron (ferrite), the branch EC to a separation of carbide Fe_3C (cementite), and the horizontal branch to a simultaneous separation of the two constituents in alternating layers (pearlyte). In other words, steel above BEC is a solid homogeneous solution of the carbide Fe_3C in an allotropic form of iron: during slow cooling that solution allows the deposition either of iron or of Fe_3C, according as to whether it is saturated with one or the other; and in this way it reaches a certain composition, that of the eutectic alloy, which remains

always the same, regardless of the original amount of carbon present, exactly as in the case of liquid solutions; the allotropic transformation plays here a part identical to that of solidification. Slowly cooled steel, therefore, will be made up of a mixture of ferrite and pearlyte (Fig. 7), of pearlyte alone (Frontispiece, Fig. 8), or of a mixture of pearlyte and cementite (Frontispiece, Fig. 9), according as to whether the carbon-content is inferior, nearly equal or superior to
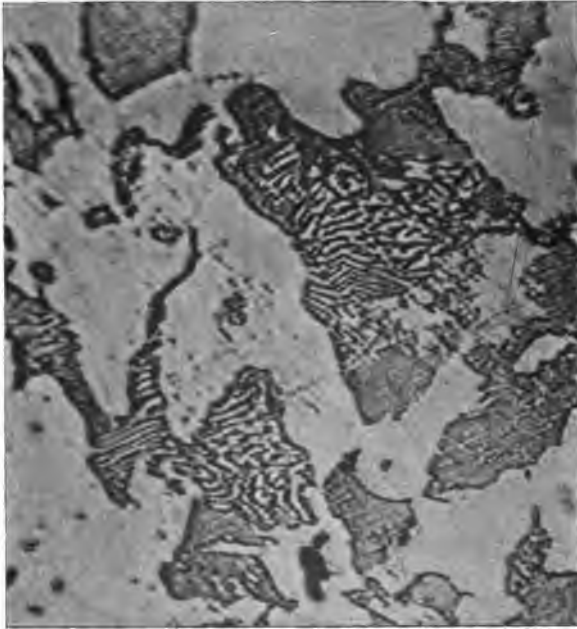
FIG. 7. Forged Steel (0.45 per cent C).
Combined polishing and etching. Magnified 1000 diameters.

the amount present in the eutectic alloy, which amount, however, may vary in the presence of other foreign substances. And thus Dr. Sorby's observations are found to fit so exactly the thermal phenomena that the one could have led to the foretelling of the other, had the theory of solutions been known earlier.

If, instead of allowing the steel to cool slowly, it is quenched in a cold liquid, the transformations which would

have taken place during slow cooling are suppressed, at least in part, having been denied the time to take place in the range of temperature where they are possible.   The carbon keeps partially its condition of dissolved carbon which it possessed at a high temperature : it is said that it remains in the condition of hardening carbon; and as the existence of a dissolved body supposes that of a dissolvent, it must seemingly follow, although the idea is energetically opposed, that the iron also retains partially an allotropic form.   The theory of hardening, such as it has been brilliantly formulated by Prof. Åkerman, remains nevertheless standing : modern investigations have enlarged and completed it, without destroying it.

Those phenomena leave their mark in the structure.   If the metal be hardened above the curve BEC, as suddenly as possible, in ice-water for instance, ferrite, pearlyte and cementite disappear.   Two cases must be considered according to the carbon-content : whether it is inferior or superior to that of the eutectic alloy.   As an instance of the first let us quench a piece of steel containing 0.45 per cent of carbon, at 1050° C.   The origin of the hardening is then represented by the point M, Fig. D.   We find a constituent, probably homogeneous, made up of needles, parallel in the same region, but which frequently cross each other along three principal directions (Fig. 10).   It is called martensite.   The needles of the martensite, the other conditions remaining the same, become smaller and less distinct as we approach the composition of the eutectic alloy; its hardness increases simultaneously up to its maximum.   Above that point the metal does not remain homogeneous.   A steel with 1.50 per cent of carbon, quenched at 1050° C. (point N of Fig. D.) in ice-water, breaks up into two constituents (Fig. 11).   One of them, austenite (the light portion in the photograph), possesses the unexpected property of being soft enough to be scratched by a sewing-needle : hardness diminishes, therefore, with the carbon-content, above a certain limit.   If the steel is allowed to cool below BEC before quenching, remaining, however, above A_1E, the constituents which had been isolated during cooling, before the quenching temperature was reached, will, of course, be found in the quenched metal.   A steel containing 0.30 per cent of carbon,

for instance, quenched at 720° (point O in Fig. D.), will exhibit some white ferrite by the side of the striated martensite; a steel with, say, 1.24 per cent of carbon, quenched at 735° (point P of Fig. D.), will contain some cementite, standing in relief with regard to the surrounding martensite. Below A_1E the structure has been formed; quenching from a point in that region will have no effect.

Bronzes. — The knowledge of bronzes is much less advanced than that of steel. The complete curve of fusibility has been determined by Mr. Stanfield, the curve of electro-

FIG. 10. Forged Steel.
Reheated to 825° C. and quenched at 720° C.
Combined polishing and etching.
Magnified 1000 diameters.

FIG. 11. Cemented (Blister) Steel (1.50 p. c. C).
Reheated to 1050° C. and quenched in ice-water.
Combined polishing and etching.
Magnified 1000 diameters.

motive force by Laurie, of electric conductivity by Lodge, of thermal conductivity by Calvert and Johnson, of hardness by Martens, of induction (by Hughes' balance) by Roberts-Austen, of resistance to tension and of elongation by Thurston. Several of those curves seem to indicate the existence of definite compounds $SnCu_3$ and $SnCu_4$, not to mention isolated perturbations. Mr. Behrens, through the study of their microstructure, was led to the notion of definite compounds more numerous still, and Mr. Le Chatelier believes to have separated $SnCu_3$ by proximate chemical analysis. But the

alloy of that composition presents two evolutions of heat. As a matter of fact, there is, possibly, not a single conclusion drawn from a series of experiments which is not in contradiction with the conclusions drawn from another series, or at least impaired by them. When one tries to conciliate the divergences, one is faced by inextricable difficulties, and the writer will not venture to increase the number of premature interpretations. The appearance of the curve of fusibility alone illustrates the complexity of the question: certain alloys have three and even four points of transformation or of solidification, whose positions and, sometimes, existence may be related to the rate of cooling. Fortunately, the solution of the problem may now be undertaken, owing especially to micrographic analysis which, alone, furnishes as many equations as there are unknown quantities, and which has already given in the hands of Messrs. Guillemin, Behrens and Charpy very interesting results. The solution is now only a question of time, of patience and of method.

Influence of Pressure. — In the foregoing we have not considered the pressure to which the metal may be subjected, either during the process of forging, or simply during cooling on account of the contraction of the outside layers which cool first. One effect of pressure consists in displacing the points of transformation, raising or lowering them according to the sign of the accompanying change of volume. That effect is not very conspicuous in the case of the melting-points, but seems to be much more marked in the case of the points of molecular transformations. Messrs. Mallard and Le Chatelier have, in this way, lowered more than 100 degrees the isomeric modification of iodide of silver. Mr. Roberts-Austen has lowered by the same means the recalescence, and it is likely that pressure, caused first by contraction, then by the change of state and of volume of the iron, plays an important part in hardening, as is thought by Prof. Åkerman.

Pathological Metallography.

This branch of metallography deals, as its name indicates, with what might be called the diseases of metals.

Fig. 12 shows a net-work of cracks in a steel quenched at

too high a temperature. Fig. 13 exhibits an inclusion of slag in steel, after mere polishing. These inclusions do not, in reality, occur frequently: they are not very troublesome when the grains of slag are small and disseminated; they may become very injurious when the slag forms layers of some magnitude near the outside surfaces, for they constitute then an enticement to rupture, which, once started, is liable to spread slowly from place to place. According to Mr. Arnold, sulphur, present as sulphide of iron, gives rise to similar inclusions.

FIG. 12. Forged Steel (1.24 per cent C).
Quenched at a white heat.
Polished on a plane surface.
Magnified 20 diameters.

FIG. 13. Slag in Steel.
Polished on a plane surface.
Magnified 1000 diameters.

Mr. Stead has recently shown, through an ingenious device, the influence of these little filaments in a malleable metal. For that purpose he bends the metallic plate, which has been previously polished and developed so as to reveal its structure, until rupture begins. It is readily seen, then, that the lines of rupture follow the slag in puddled iron, the cementite in cementation-steel, the phosphide of tin in an alloy of tin and phosphorus.*

* A résumé of Mr. Stead's paper is printed in the present number of *The Metallographist.* — ED.

The foreign substances and their chemical combinations do not always form, in metals and alloys, those independent net-works, sometimes useful, sometimes injurious, whose influence upon the mechanical properties may be so great. They may remain invisible and dissolved, modifying the condition and the qualities of the metallic mass in its entire bulk.

At all events, the structure acquired after a certain rate of cooling may always be disturbed by an elevation of temperature, which redissolves the segregated compounds or sets in motion the dissolved substances.

It is not known *a priori* whether such changes will be good or bad in a given case. But it must be remembered that the structure, and, therefore, the properties of a refractory metal may be extensively modified by a reheating to a relatively low temperature, in presence of a slight proportion of certain impurities. The fact deserves serious consideration.

The distinction between morbid accidents and physiological phenomena is not always as visible as in the preceding instances. It may result from a convention established by experience. If a certain mechanical and thermal treatment gives to a certain metal the best possible qualities, the metal so prepared may be regarded as healthy. And, inversely, the metal prepared by different processes may be regarded as diseased.

Take a steel with 0.45 per cent of carbon which has been reheated, after forging, respectively to 750°, 1015° and 1390° C. The three samples are made up of a mixture of ferrite and pearlyte, but how very different they are! In the first case both constituents are present in small-size particles irregularly mixed; in the second case the pearlyte shows a tendency to form polyhedric grains which are surrounded by ferrite in the shape of a continuous and ramified net-work; in the third case this structure is more pronounced yet, the grains of pearlyte having become so large that under a magnification of 100 diameters the microscopic field does not cover a whole grain. The appearance of the structure and the absolute dimensions of the grains are, therefore, as has been shown especially by Mr. Sauveur, characteristic of the thermal treatment. Microscopic examinations will make it possible to

ascertain the heat-treatment to which the metal was sub-
jected, and to correct it when necessary.

Having spoken of the diathesis and of the diseases of
metals, it remains to improve our means to avoid or to cure
them, as far as possible, in order to insure the solidity and
durability of our constructions. Such is the common aim of
all the members, metallurgists or builders, of the Inter-
national Association for the Testing of Material. To reach
that end, metallography offers them a new means of diagnosis,
whose methods improve every day, and whose utility appears
more and more manifest.

THE MICROSTRUCTURE OF STEEL AND THE CURRENT THEORIES OF HARDENING.

A PAPER bearing the above title was presented by Mr.
Albert Sauveur to the American Institute of Mining
Engineers at the Colorado meeting, in September, 1896. The
discussion of the paper was postponed until the following
meeting, which took place last February in Chicago, and was
participated in by Messrs. Ledebur, Hadfield, Scott, Jenkins,
Arnold, Roberts-Austen, Hibbard, P. H. Dudley, E. D.
Campbell, Howe and Osmond.

The author first recalls the meaning of the "critical
points" of iron and steel. If a piece of steel containing, say,
0.50 per cent or more of carbon be heated to a high tempera-
ture and then allowed to cool slowly, the cooling proceeds at
first at a uniformly retarded rate until a temperature of about
700° C. is reached, when there is a sudden "retardation" in
the fall of the temperature, indicating an evolution of heat,
often so considerable as to cause a momentary stop in the
cooling, or even an actual rise of the sensible temperature, —
a "recalescence" of the cooling metal. After this retardation
the fall of temperature resumes its normal rate, which is con-
tinued until atmospheric temperature is reached. This retar-
dation during the cooling, which indicates that some impor-
tant change, evolving heat, is taking place within the metal,
is called a "critical point." Mr. Osmond, who was the first

to determine accurately, by means of the excellent pyrometer of Mr. Le Chatelier, the position and magnitude of the critical points, adopted Chernoff's notation, and designates the critical points by the letter A.

In heating, as would be expected, there is a reverse phenomenon, an absorption of heat causing a retardation in the rise of temperature. To distinguish the critical point which occurs in cooling from that which occurs in heating, the former is called Ar, the latter Ac. The two retardations, however, do not take place at the same temperature, the critical point Ac being situated some 30° higher than Ar.

Mr. Howe has shown conclusively that, in order to induce the retardation Ar, or rather the change which such retardation implies, the steel must first be heated past the point Ac; and reciprocally, the change which occurs at Ac cannot take place unless the steel has first been cooled to a point below Ar. Clearly, therefore, the retardations Ar and Ac, although not taking place at exactly the same temperature, are simply the opposite phases of the same phenomenon. The change at Ar is the reversal of that at Ac.

Howe and Osmond have shown that by hastening the cooling the critical point Ar is proportionally lowered until, when the cooling is sufficiently rapid, as in quenching, there is no retardation; the change Ar does not take place. Hence certain conditions which existed above Ar are retained by quenching; and to this retention the various theories attribute the hardness of quenched steel. It is only in regard to the nature of what is thus preserved by sudden cooling that they differ. The heat of the retardation Ar remains latent in hardened steel, and can be made apparent, according to Mr. Osmond, by dissolving the metal in double chloride of ammonium and copper, when it evolves more heat than unhardened steel. This latent heat is also liberated during tempering, and produces an acceleration in the rate of heating.

High carbon-steels and those of medium hardness have only one critical point. Such is not the case, however, with softer steels, which exhibit, on cooling or heating, two or three critical points. To distinguish these, they are called respectively Ar_3, Ar_2, Ar_1, and similarly, in heating, Ac_3, Ac_2, Ac_1.

Like the single retardation of hard steel, the multiple retardations of soft steel indicate reversible changes. Ac_3 and Ac_1 occur at a temperature somewhat higher than Ar_3 and Ar_1, while Ac_2 and Ar_2, on the contrary, take place at nearly the same temperature. Certain impurities, especially manganese, nickel, chromium and tungsten, lower the critical points very decidedly. Manganese and nickel, when present in sufficient quantity, apparently eliminate them (probably by lowering them below the atmospheric temperature). It is also probable, roughly speaking, that the purer the steel, the longer will the three critical points remain separated, as the percentage of carbon increases.

By critical points, therefore, is meant those retardations which occur during the heating and cooling of a piece of steel, and which indicate that some important changes, absorbing or evolving heat, are in progress; which changes, as will be seen, greatly affect the chemical, physical and mechanical properties of the metal.

The purpose of the paper was first, to describe at some length the changes of microstructure which occur, during slow cooling, in steels containing various amounts of carbon, and secondly, to examine what bearing, if any, such structural changes as occur at the critical points, have upon the current theories of hardening.

The author calls attention to the importance of properly developing the structure of the specimens to be examined through the microscope, and recommends two methods of etching as equally good : the iodine method, suggested by Mr. Osmond and which consists in attacking the polished surface with tincture of iodine, and the concentrated nitric-acid process, as practiced by himself, which consists in dipping the sample in nitric acid of 1.42 sp. gr., followed by a rapid washing under an abundant stream of water. Polishing in relief upon a yielding support, consisting of a block of soft wood, upon which is stretched a piece of parchment thoroughly soaked with water and covered with a very little rouge, develops the structure of certain samples without requiring any further treatment, and affords a good means of judging the relative hardness of some components. The microscopic constituents of steel are then described at length.

All carbon-steels, whether quenched or slowly cooled, are made up of one or more of four primary constituents, which have been called respectively : *ferrite*, *cementite*, *pearlyte* and *martensite*. The three first names were proposed by Mr. Howe, the last by Mr. Osmond.

Ferrite is iron free from carbon. Whether it is free also from the other impurities usually present in steel has never been conclusively shown. Indeed, it is quite probable that the grains of ferrite are sometimes impregnated with impurities. Ferrite presents three principal modes of occurrence:

1. When present in considerable quantity, as in soft steel slowly cooled or quenched below the critical range, it segregates in relatively large masses, and crystallizes in polyhedric grains, which are interfering crystals of the isometric system, mostly cubes and octohedra (see Plate I., Figs. 2, 3, 4). In the drawings the ferrite is left white, the black net-work showing the outlines of the grains.

2. In steel of medium hardness, which has been slowly cooled from a high temperature, the ferrite, present only in small quantity, forms a membrane of varying thickness enveloping the grains of pearlyte. A section cut at any angle will therefore exhibit a net-work structure, the pearlyte forming the meshes. If such steel, however, be forged until a relatively low temperature is reached, or if it be reheated to a low temperature (a little above the critical range), the pearlyte and ferrite are more thoroughly mixed in a somewhat confused manner, presenting an amorphous appearance.

3. Ferrite forms a structural element of pearlyte, which, as will be seen presently, is made up of an intimate mixture of ferrite and cementite. To distinguish it from this variety, the ferrite, which in the structure exists by itself in segregated masses, will here be called structurally free, or segregated ferrite.

Structurally free ferrite forms, of course, the totality of carbonless iron. As the carbon-content increases, the free ferrite diminishes, until at about 0.80 per cent of carbon it entirely disappears, the steel being then wholly made up of pearlyte (see Fig. 4 and Plate I., Fig. 12).

The etching of the polished sections with iodine or nitric acid leaves the ferrite white and brilliant, and develops the

Fig. 4
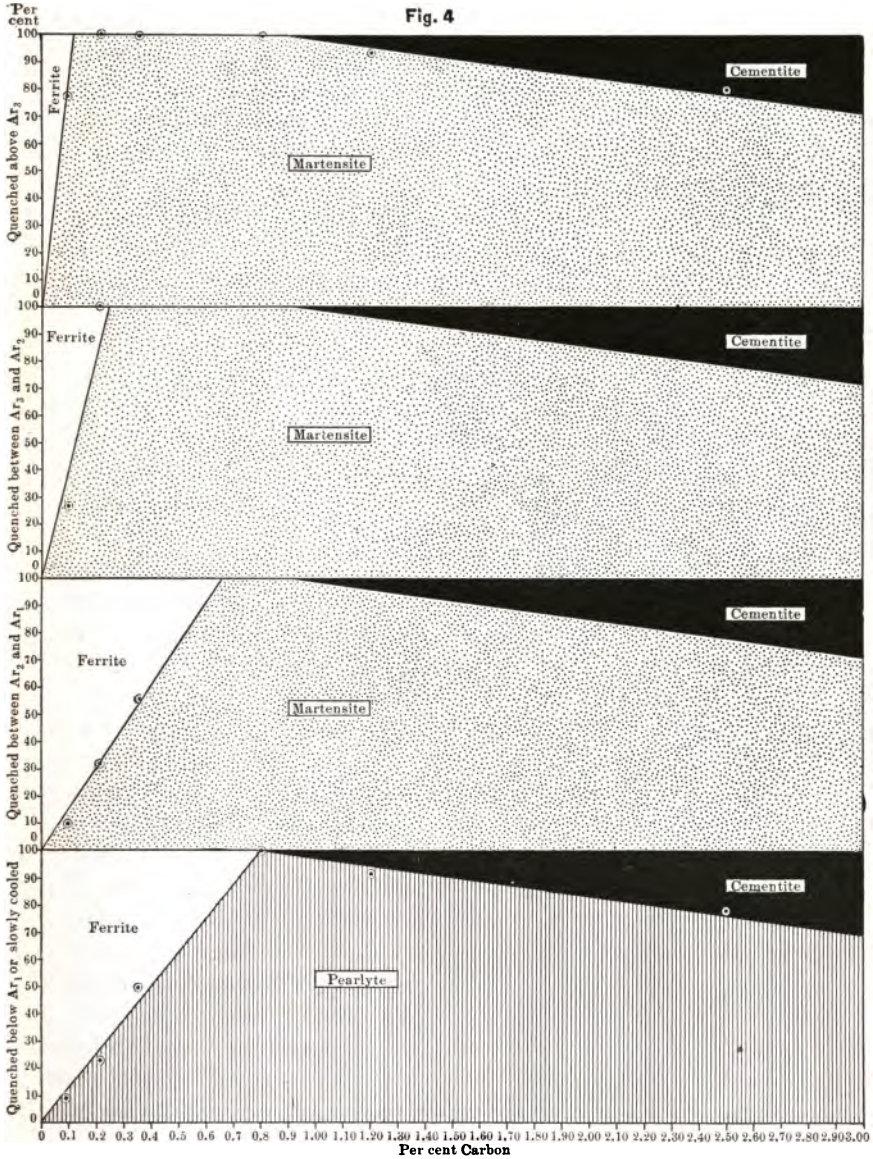
MICRO-STRUCTURAL COMPOSITION OF STEEL QUENCHED ABOVE, BETWEEN,
AND BELOW THE CRITICAL POINTS

● Points actually determined

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joints between the grains. On etching more deeply, however, some of the grains are slightly colored or take a mottled appearance, while others remain bright. Ferrite being the softest of all the constituents in the field, it is more easily and quickly worn away by polishing, so that under the microscope all the other constituents stand in relief with regard to it; this constitutes an additional means of identifying it.

Cementite. — This is iron combined with cement-carbon, i.e., carbon as it exists in unhardened steel. It is a carbide, answering to the formula Fe_3C. As early as 1885, Abel and Müller, working independently, ascertained the presence in unhardened steel of such a carbide; and the more recent researches of Arnold and Read have fully confirmed their conclusions, so that there is now hardly any possible doubt concerning the chemical composition of cementite. In steel containing much manganese, however, it is very probable that this constituent is a double carbide of iron and manganese.

Like ferrite, cementite occurs:

1. In segregated masses in very hard steel, but it always remains structureless. In the drawings of Plate I. the cementite is shown in black, to distinguish it from the ferrite, which is left white.

2. As a very thin membrane, around the grains of pearlyte, when present in small quantities and under certain conditions (see Plate I., Fig. 14).

3. As a structural element of pearlyte.

Cementite remains bright and brilliant, even after repeated etchings of iodine or nitric acid. It has a more metallic luster than ferrite; and, to an experienced eye, this appearance alone will suffice to identify it. While ferrite is the softest, cementite is the hardest of the constituents, so that it stands in relief relatively to the others, especially if the polishing is finished on a soft, yielding support. Moreover, free ferrite has a granular structure, while cementite is always structureless. Again, cementite cannot be scratched by a needle, while the soft ferrite is easily marked in this way. Structurally free cementite is not found in soft or medium-hard steel. It begins to appear in steel containing about 0.90 per cent of carbon, and then increases in quantity proportionally to the carbon-content. In steel of 2 per cent carbon it forms about 23 per

cent of the mass (see Fig. 4 and Plate I., Fig. 16). Structurally free ferrite and structurally free cementite never exist together in the same steel. The former is the associate of pearlyte in soft and medium-hard steel, the latter the associate of pearlyte in highly carburetted steel (see Fig. 4).

Pearlyte. — As already stated, pearlyte is not, strictly speaking, an elementary constituent of steel; but it is, nevertheless, a very distinct one, and should be treated as such rather than as a mere mixture of ferrite and cementite.

A magnification of at least 300 diameters is required to resolve satisfactorily the structure of pearlyte. We find then, as first pointed out by Mr. Osmond, that it is necessary to distinguish between lamellar and granular pearlyte. The lamellar variety is best found in steel very slowly cooled from a high temperature, and especially in annealed steel. The longer the annealing, the more pronounced the character of the structure. It is called lamellar, because it is made up of very thin plates or lamellæ, alternately of ferrite and cementite. This structure gives rise, under the microscope, to a beautiful play of color, strongly suggestive of mother-of-pearl. Dr. Sorby, who first discovered it, called it the pearly constituent, and Mr. Howe pearlyte.

The presence of well-defined lamellar pearlyte is certain proof that the steel has been annealed or cooled slowly and undisturbedly from a high temperature. The granular variety is found in steels that have been forged down to a comparatively low temperature, or which have been reheated to a low temperature. As the name indicates, it is somewhat granular in appearance, consisting of a mixture of small irregular grains of cementite and ferrite. Pearlyte is always present in unhardened steel; at first in a very small quantity, but increasing rapidly with the carbon-content. When the steel contains about 0.80 per cent of carbon, the whole mass consists of pearlyte. With further increase of carbon the amount of pearlyte diminishes, being gradually replaced by structurally free cementite (see Fig. 4).

Pearlyte is colored dark both by iodine and by nitric acid. It always forms the dark constituent of unhardened steel.

As just pointed out, in steel with about 0.80 per cent of carbon, pearlyte is·the sole constituent. Prof. Arnold very

properly calls this point "the saturation-point" of steel; and he finds that in steel containing very little impurity, besides carbon, about 0.90 per cent of carbon is required for saturation, i.e., that not until then does all the structurally free ferrite disappear. With commercial steels, however, such as those used in connection with the present investigation, containing from 0.40 to 1.00 per cent of manganese, and from 0.75 to 1.25 per cent of total impurities, the saturation-point is very near 0.80 per cent of carbon.

It is quite certain that the purer the steel the more carbon is required to saturate it. This, no doubt, is partly due to the fact that an impure steel contains less iron to be saturated, and also to the presence of considerable manganese, which, forming a double carbide, helps to saturate, further reducing thereby the necessary amount of carbon. The pearlyte of commercial steel therefore contains about 0.80 per cent of carbon, or about 12 per cent of cementite (Fe_8C), and 88 of ferrite; roughly, 1 part of cementite to 7 parts of ferrite.

The structure of unhardened steel is explained as follows: The carbon present in the steel unites with a portion of the iron to form Fe_8C or cementite. The ferrite and cementite then unite structurally in definite proportions to form pearlyte, leaving, as the case may be, an excess either of ferrite or of cementite, the former in soft steel, the latter in highly carburetted steel, as shown in Fig. 4. Knowing the compositions of cementite and pearlyte, the theoretical microstructural composition of any carbon-steel can easily be calculated. If, for instance, the steel contains 0.50 per cent of carbon, we know that this amount of carbon will unite with a portion of the iron to form cementite, or Fe_8C ($6.67 \, C + 93.33 \, Fe$) in the following proportion:

$$C. \quad Fe_8C. \quad C.$$
$$6.67 : 100 = 0.50 : x,$$

yielding therefore 7.50 per cent cementite. This cementite unites structurally with an additional amount of iron, forming pearlyte ($12 \, Fe_8C + 88 \, Fe$), as follows:

$$Fe_8C. \quad Pearl. \quad Fe_8C.$$
$$12 : 100 = 7.50 : x,$$

or 62.50 per cent of pearlyte. The balance of the steel, or 37.50 per cent, is made up of structurally free ferrite. If the

steel contains more than 0.80 per cent (say 1.20, for instance) of carbon, we have an excess of cementite. The composition can then be determined as follows: 1.20 per cent of carbon yields 18 per cent of cementite. This leaves 82 per cent of free iron, which will unite with part of the cementite to form pearlyte, as follows:

$$\text{Fe.} \quad \text{Fe}_3\text{C.} \quad \text{Fe.}$$
$$88 : 12 = 82 : x,$$

or 11.18 per cent of cementite, leaving therefore 6.82 per cent of structurally free cementite. Hence the structure of such steel is made up of 93.18 per cent of pearlyte and 6.82 per cent of structurally free cementite.

These figures would probably be absolutely correct, if the steel contained nothing but iron and carbon. The impurities always present in commercial steel, however, will necessarily alter them — which renders these calculations only approximate. In the following table, the microstructural composition of unhardened steel, containing various amounts of carbon, has been calculated in this way, the decimals being omitted.

TABLE I. — *Theoretical Microstructural Composition of Unhardened Carbon-Steels.*

CARBON. PER CENT.	MICROSTRUCTURAL COMPOSITION. PER CENT.			CARBON. PER CENT.	MICROSTRUCTURAL COMPOSITION. PER CENT.		
	Pearlyte	Ferrite	Cementite		Pearlyte	Ferrite	Cementite
0.	0	100	0	1.30	91	0	9
0.10	12	88	0	1.40	90	0	10
0.20	25	75	0	1.50	88	0	12
0.30	37	63	0	1.60	86	0	14
0.40	50	50	0	1.70	85	0	15
0.50	62	38	0	1.80	83	0	17
0.60	75	25	0	1.90	81	0	19
0.70	87	13	0	2.00	80	0	20
0.80	100	0	0	2.10	78	0	22
0.90	98	0	2	2.20	76	0	24
1.00	97	0	3	2.30	74	0	26
1.10	95	0	5	2.40	73	0	27
1.20	93	0	7	2.50	71	0	29

Martensite. — Martensite is that constituent which exists at a high temperature, and being retained by sudden cooling

confers hardness upon quenched steel. While we know with reasonable certainty the composition of ferrite, cementite and pearlyte, we know very little about the true nature of martensite. Indeed, if we could discover its composition, the hardening of steel would no longer be an unsolved problem. Each theory which has been advanced to explain the hardening of steel has attributed to martensite the composition demanded by that theory. Of its real composition, however, we have no direct evidence.

Martensite contains iron and carbon, but not in definite proportions like pearlyte; the amount of carbon it contains varying from 0.12 per cent in very soft steel, quenched above the critical range, to 0.90 per cent in hard steel. It forms about 75 per cent of very mild steel quenched (the balance being ferrite), while it constitutes the whole bulk of hardened steel containing from 0.22 to 0.80 per cent of carbon. In more highly carburetted steel some structurally free cementite is found besides the martensite (see Fig. 4 and Blate I.). As might be expected, therefore, the hardness of martensite varies greatly. In its most dilute form (when it contains the greatest proportion of iron) it is relatively soft, while when highly carburetted, it becomes intensely hard, although never as hard as cementite.

The composition of martensite will be discussed at greater length a little farther on.

Martensite is colored both by iodine and by nitric acid; but the intensity of its coloration varies with the degree of carburization. When much diluted, as in very soft steel quenched above the critical range (Plate I., Fig. 1), it assumes a light yellowish tint, which increases in depth with. the increase of carbon. Highly carburetted martensite (i.e., the martensite of high-carbon steel) is colored much darker by the etching — as dark and even darker than pearlyte under similar treatment. Dilute martensite is easily distinguished from pearlyte by its light yellow color. With the more carburetted or concentrated variety, the color alone is no longer a sure guide, and we must then differentiate them by their structure. If the pearlyte is lamellar, no confusion is possible, for its peculiar structure will readily identify it. With granular pearlyte the differentiation is more difficult, and the

structure must then be closely examined. Martensite, as Mr. Osmond has remarked, often presents groups of parallel needles, or rectilinear fibers, which cross each other frequently.

It should be remembered that very high power is necessary to resolve the structure of martensite, and even then the details are so minute and often so confused that what is revealed teaches us little with regard to its nature. The writer finds strong indications, however, that martensite, like pearlyte, is made up of two components differing in hardness.

To sum up, all unhardened steels are composed of pearlyte alone, or pearlyte associated either with ferrite or cementite. All hardened steels are composed of martensite alone, or martensite associated with ferrite or cementite.

Mr. Osmond, in his paper already referred to, describes two additional constituents, which he calls, respectively, sorbite and troostite. They are "transition-forms," as Mr. Osmond calls them, having but a short existence in the structural changes induced in steel by heat-treatment. Mr. Osmond finds that on etching with iodine, a high-carbon steel reheated to a little above the critical range, part of the pearlyte is either entirely colored, or only as to some of its lamellæ, and as both ferrite and cementite should remain bright after such a treatment, he infers that we are here in the presence of a new constituent, *sorbite*, and that the pearlyte of such steel is made up of pearlyte and sorbite, or cementite and sorbite, or even of two sorbites differently colored. He supposes that it contains some hardening carbon, and that it represents a *zone of transition* between the ferrite and cementite in unhardened steel, and between cementite and martensite in quenched steel.

The constituent *troostite* Mr. Osmond finds in steel quenched during the critical points, between the martensite and the ferrite. It is a "transition-form" between these two constituents. Nothing is said regarding its chemical composition.*

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* Mr. Osmond has called attention more recently to still another micro-constituent of steel, which he terms *austenite*. It is to be found only in steel containing over 1 per cent of carbon, and quenched very rapidly from a high temperature, in a cold mixture. Under these conditions the proportion of austenite increases with the carbon up to about

The author then studies the microstructure of quenched steel, in order to ascertain whether there were any perceptible changes corresponding to the critical points, and, if any, to determine their nature. For that purpose a number of steel bars containing different amounts of carbon were heated considerably above the critical range, and quenched, after slow cooling, from various temperatures above, between and below the critical points. In this way the structural arrangement which prevailed at the quenching-temperature was retained in the cold metal, and it was possible to judge of the changes of structure occurring in steel during slow cooling, and to ascertain what relations they bear to the critical points.

Six samples of steel were accordingly selected, containing respectively 0.09, 0.21, 0.35, 0.80, 1.20 and 2.50 per cent of carbon. They were all commercial steels, containing from 0.40 to 0.90 per cent of manganese, and from 0.60 to 1.00 per cent of total impurities (carbon not included).

Several bars of each series were heated well past the critical range and allowed to cool partially before quenching, one bar being quenched above Ar_3, another between Ar_3 and Ar_2, the next between Ar_2 and Ar_1, and the last below Ar_1.

The structures of these various samples were drawn from the microscope, being uniformly magnified 250 diameters and arranged comprehensively in Plate I. In steels which do not possess the upper retardation Ar_3, no change of structure takes place above Ar_2, and in steels which have only the lower retardation Ar_1 there is only one change of structure. This

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1.60 per cent of C, when it constitutes nearly 50 per cent of the mass (see Fig. 11, page 23). With further increase of the carbon-content the proportion of austenite diminishes. The amount of austenite also increases with the quenching-temperature. "The properties of this constituent," Mr. Osmond says, "closely recall the properties of steel with 12 or 13 per cent of manganese, and steel with 25 per cent of nickel. Its most salient property is that of being scratched by a darning-needle or by apatite. . . ." From the above facts it would appear that Fig. 4 of the present paper, which indicates the presence of martensite and cementite only in quenched high-carbon steel, is at fault. It must be remembered, however, that austenite appears *only* when the metal is *very* suddenly cooled in a freezing mixture, which was not the case with the samples experimented upon here. In the industrial treatment of steel such conditions are never encountered, and Fig. 4 represents correctly, it is thought, the structural composition of steel quenched as is customary in practice. — ED.

explains the arrangement of the drawings. The areas occupied by the various constituents were measured with the planimeter, and their percentages are tabulated in Table II.

The paper gives a short description of the manner in which these measurements are conducted. The results shown in Table II. were obtained from areas at least twice as large as those reproduced in Plate I. As an illustration, let us take the bar containing 0.09 per cent carbon and quenched between Ar_3 and Ar_2. The actual field measured is shown in Fig. 3, page 43. For the sake of simplicity, the joints of the grains of ferrite are not shown in the drawing.

TABLE II. — *Microstructural Composition of Some Quenched Carbon-Steels.*

Steel No.	Carbon. Per Cent.	Quenched Above Ar_3. Per Cent in Vol.*			Quenched Between Ar_3 and Ar_2. Per Cent in Vol.			Quenched Between Ar_2 and Ar_1. Per Cent in Vol.			Quenched Below Ar_1 or Slowly Cooled. Per Cent in Vol.		
		Mart.	Fer.	Cem.	Mart.	Fer.	Cem.	Mart.	Fer.	Cem.	Pearl	Fer.	Cem.
1	0.09	77	23	0	27	73	0	11	89	0	10	90	0

Quenched Above Ar_2. Per Cent in Volume.

Steel No.	Carbon. Per Cent.	Martensite.		Ferrite.		Cementite.		Mart.	Fer.	Cem.	Pearl	Fer.	Cem.
2	0.21	100		0		0		31	69	0	23	77	0
3	0.35	100		0		0		56	44	0	50	50	0

Quenched Above Ar_1. Per Cent in Volume.

Steel No.	Carbon. Per Cent.	Martensite.		Ferrite.		Cementite.		Pearl	Fer.	Cem.
4	0.80	100		0		0		100	0	0
5	1.20	94		0		6		92	0	8
6	2.50	80		0		20		77	0	23

It is proposed to ascertain the total area occupied by the martensite. If we were to measure each little area independently, the work would be very long and tedious; and, besides,

---

* If a body containing a great many particles is cut by a plane, a certain number of the particles will be intersected, and the ratio of the sum of these small areas to the total area of the section is practically equal to the ratio of the volume of the small particles to the total volume of the body. Mathematically, however, the two ratios are equal only if the number of particles is infinite and the uniformity of distribution perfect.

Quenched
above
Ar₃

Fig. 1

Quenched
between
Ar₃ and Ar₂

Fig. 5

Fig. 8

Quenched
between
Ar₂ and Ar₁

Fig. 2
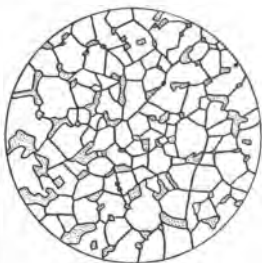
Fig. 3

Fig. 6

Fig. 9
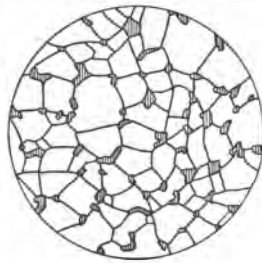
Quenched
below Ar₁
or
slowly cooled

Fig. 4
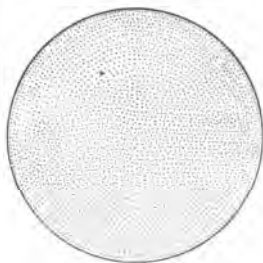
Fig. 7
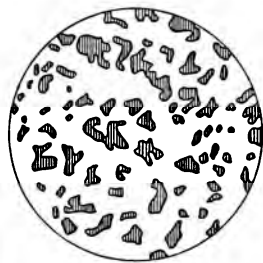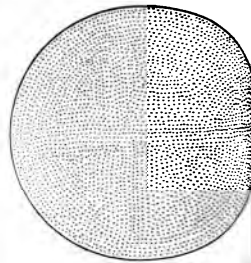
Fig. 10

Ferrite Martensite

MICRO-STRUCTURE OF STEEL QUENCHED ABOVE
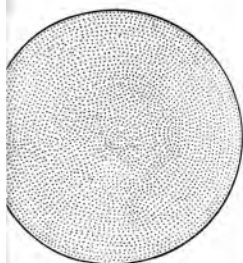
Fig. 11
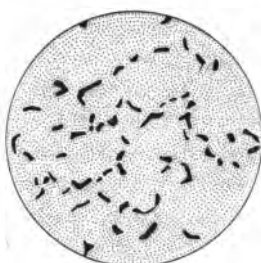
Fig. 13
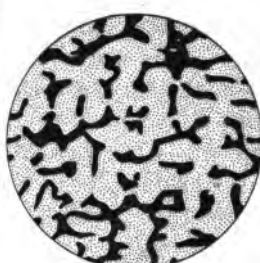
Fig. 15
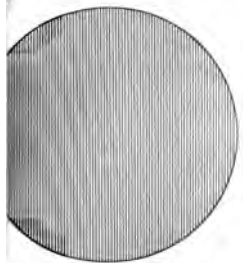
Fig. 12
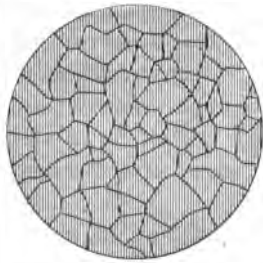
Fig. 14
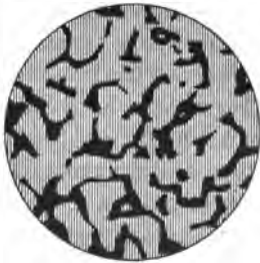
Fig. 16

rlyte   ■ Cementite

EEN AND BELOW THE CRITICAL POINTS

the great number of readings and adjustments of the planim-
eter required would introduce a serious source of error. To
simplify the operation and greatly reduce the possible error,
all the small areas are united in a continuous chain, as shown
by the dotted lines, in such a way that starting from the point
A, and passing from one grain to the other, we finally reach
the point E, thus coming in contact with all the small areas
in our travel. We then proceed as follows: The planimeter
set at zero is placed at A, and we start, moving it in the
direction indicated by the arrow, as if to measure the small
area; when we reach the point B, however, we pass over to
the next grain, following along the dotted line BC; from the
point C we pass to D, following the outline of that grain;
from D to the next area; and so on until we reach the point
E on the last small area. We then follow the whole outline
of this grain, which brings us back to E, and from E we pro-
ceed on our return-trip, again passing from one grain to the
next in the reverse order, but this time going over that por-
tion of the outline of each grain which we had previously not
traveled over. It is evident that by proceeding in this way
we have followed with the planimeter the complete outline of
each grain of martensite. The error introduced by going over
the dotted lines in one direction is exactly neutralized by
going over them in the opposite direction on our return-
journey, and the reading of the planimeter gives the total
area of the martensite. This method is quick, requiring but
one adjustment of the planimeter and one reading; it is
accurate, there being no trouble in checking the results.

The structural compositions of the various samples were
ascertained in this way, and the results shown in Table II. were
plotted in Fig. 4 which gives a graphical representation of the
microstructural composition of any carbon-steel quenched
either above, between or below the critical points, as well as
when slowly cooled, and will assist in understanding the
nature and magnitude of the structural changes which occur
at those points.

As already mentioned, the amount of impurities (besides
carbon) have some influence upon the relative proportions of
the microscopic constituents. In very pure steels, for instance,
the saturation-point is near 0.90 per cent; so that we cannot

from Fig. 4 infer the composition of any carbon-steel with absolute accuracy; but it gives approximate results, quite satisfactory in the case of commercial steel.

The writer has repeatedly checked by planimeter-measure-

FIG. 3.
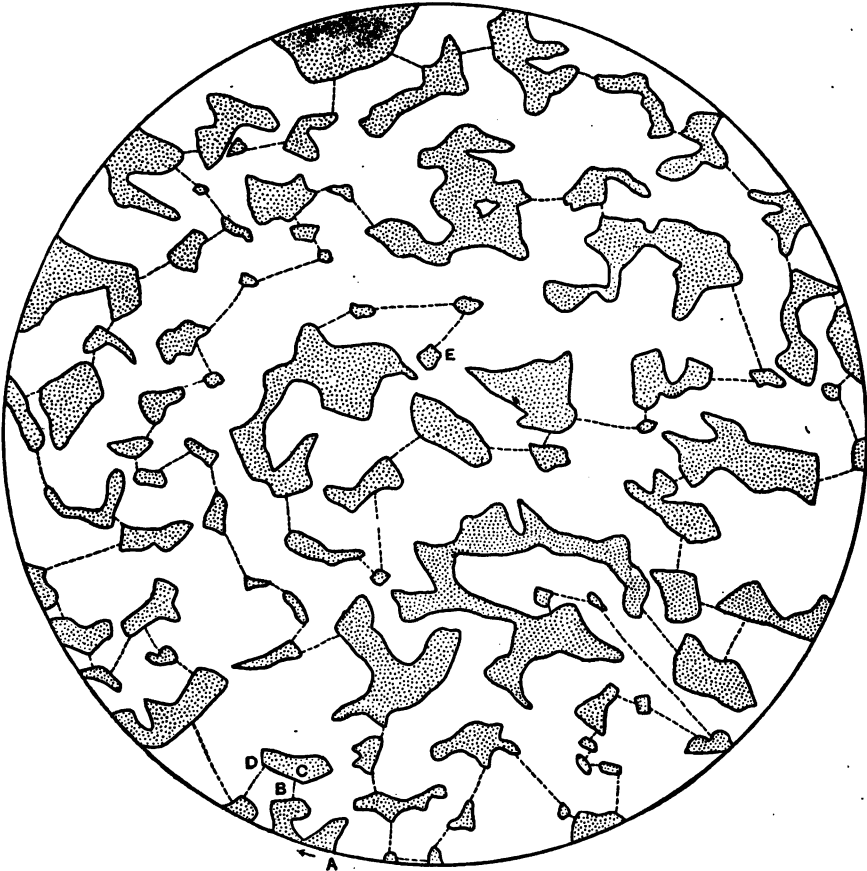
Section 0.09 = Carbon-Steel, quenched between Ar_3 and Ar_2.

ment the carbon per cent found by chemical analysis, on the assumption that pearlyte contains 0.80 per cent of carbon. To obtain comparative results, however, the steel should always be heated to the same temperature (preferably just above the critical range) previous to the microscopical examination, as

it has been found that heating to different temperatures some-what alters the volumes occupied by the pearlyte.

From the drawings of Plate I. and the figures of Table II. it is seen that *each critical point is accompanied by a marked struct-ural change.* It will be shown subsequently that the changes of structure correspond *exactly* with the retardations, begin-ning and ending with them.

The structural changes which occur in each series of steel here investigated are then examined separately.

Steel No. 1 — *Carbon*, 0.09 *Per Cent.* — When quenched above Ar_3 the steel consists of 77 per cent of martensite and 23 of ferrite. This martensite of course contains a very small proportion of carbon. It takes a light yellow color when etched with iodine or nitric acid, and is not very hard, being easily scratched by a needle. Between Ar_3 and Ar_2 the structure consists of 27 per cent of martensite distributed as irregular grains throughout a matrix of structurally free fer-rite. During the retardation at Ar_3, therefore, some 50 per cent of the martensite has been replaced by ferrite. The mar-tensite of this sample is much harder than that of the preced-ing one, and is colored quite dark by etching. It is very hard, standing prominently in relief, when the polishing is finished, upon a yielding support, and cannot be marked by a needle. Between Ar_2 and Ar_1 the amount of martensite has been reduced still further, occupying now only 11 per cent of the total mass. During the retardation Ar_2 some 15 per cent of the ferrite, which above that point was enclosed in the marten-site, has separated, bringing the amount of structurally free ferrite up to 89 per cent. When quenched below Ar_1 we find that the structure is made up of 10 per cent of pearlyte and 90 of structurally free ferrite. During the critical point Ar_1, the 11 per cent of martensite existing above that point disappears, yielding 10 per cent of pearlyte and 1 additional per cent of ferrite. This is also the structural composition of the same steel when slowly cooled, and shows that quenching below the critical range changes neither the nature nor the relative amounts of the constituents. This is true for all steels.

Steel No. 2 — *Carbon*, 0.21 *Per Cent.* — In this steel the upper critical point Ar_3 is missing; and, when quenched before the retardation Ar_2 has set in, it is made up wholly of marten-

site (Plate I., Fig. 5). This martensite is, of course, not highly carburetted, and is only lightly colored by the etching. Between Ar_2 and Ar_1 the structure is made up of 31 per cent of martensite in irregular grains, distributed throughout a matrix of structurally free ferrite (Plate I., Fig. 6). We infer from this structure that during the retardation Ar_2 some 70 per cent of ferrite previously locked in the martensite has been set free. The grains of the ferrite are not shown in this drawing; they are in all respects similar to those outlined in Figs. 2, 3 and 4 of the same plate. Below Ar_1 we find that the mass is made up of 23 per cent of pearlyte and 77 of ferrite (Plate I., Fig. 7), which shows that during the retardation Ar_1 the 31 per cent of martensite existing above that point has been changed into 23 per cent of pearlyte, setting free 8 per cent more of ferrite.

Steel No. 3 — *Carbon*, 0.34 *Per Cent.* — This steel, like the preceding one, has only two critical points, and, when quenched above Ar_2, contains only martensite (Plate I., Fig. 8), but a martensite somewhat more carburetted, therefore harder and more darkly colored. During the first retardation, Ar_2, 44 per cent of ferrite is set free, reducing the percentage of martensite to 56 (Plate I., Fig. 9). Here the martensite no longer occurs in separate grains throughout the soft iron matrix, but forms an intricate continuous mass. Below Ar_1 the steel is made up of equal masses of pearlyte and ferrite (Plate I., Fig. 10). The character of the structure remains the same as if the martensite had merely been transformed *in situ* into pearlyte, yielding also a small amount (6 per cent) more of free ferrite.

Steel No. 4 — *Carbon*, 0.80 *Per Cent.* — Here we have reached the saturation-point. The whole mass of the steel when slowly cooled or quenched below Ar_1 is made up of pearlyte (Plate I., Fig. 12). It has only one critical point, above which it is wholly composed of martensite (Plate I., Fig. 11). This martensite, which contains much carbon, is colored very dark and is extremely hard.

Steel No. 5 — *Carbon*, 1.20 *Per Cent.* — When quenched above its single critical point, this steel contains, besides a matrix of martensite, about 6 per cent of structurally free cementite, disseminated, worm-like, through the mass (Plate I., Fig 13).

Below Ar_1 the martensite has disappeared, having been replaced by pearlyte, which forms the meshes of a net-work of cementite, the latter constituent occupying about 8 per cent of the total volume (Plate I., Fig. 14).

Steel No. 6 — *Carbon*, 2.50 *Per Cent.* — The structure of this highly carburetted steel above the critical point is composed of 80 per cent of martensite and 20 of structurally free cementite (Plate I., Fig. 15). At Ar_1 the martensite is changed into 77 per cent of pearlyte, bringing the amount of free cementite up to 23 per cent (Plate I., Fig. 16).

TABLE III. — *Microstructural Composition of Steel Containing* 0.21 *Per Cent of Carbon and Quenched Above, During and Below the Critical Range.*

QUENCHING-TEMPERATURE. DEGREES C.	POSITIONS OF QUENCHING-TEMPERATURE.	MICROSTRUCTURAL COMPOSITIONS. PER CENT.		
		Martensite.	Ferrite.	Pearlyte.
880		100.	0.0	0.0
836		100.	0.0	0.0
797	Above Ar_2 - - - - -	100.	0.0	0.0
761		100.	0.0	0.0
733		100.	0.0	0.0
714	Beginning of Ar_2 - -	97.20	2.80	0.0
713		86.00	14.00	0.0
698	Middle of Ar_2 - - -	70.20	29.80	0.0
652		35.20	64.80	0.0
650	Between Ar_2 and Ar_1 -	30.80	69.20	0.0
633		32.00	68.00	0.0
626		31.50	68.50	0.0
620	Beginning of Ar_1 - -	30.00	68.40	1.60
600	End of Ar_1 - - - -	4.00	78.50	17.50
559		2.00	75.80	22.20
575		0.0	78.90	21.10
532		0.0	76.80	23.20
512	Below Ar_1 - - - - -	0.0	77.00	23.00
340		0.0	77.40	22.60
263		0.0	75.20	24.80
200		0.0	76.40	23.60

In order to show how closely the structural changes just described correspond with the retardation, Table III. and Fig. 5, already published in the *Journal of the Iron and Steel Institute*, have been reproduced here. In this investigation, 21 bars of steel No. 2 were heated to 970°C., then slowly cooled to a series of points near and within the critical range, from which they were suddenly cooled. In this manner some of the bars were quenched *during the retardations themselves*,

thus revealing the progress of the corresponding structural changes. The microstructural composition of the various bars, together with their quenching-temperature, are shown in Table III.

These percentages are plotted in Fig. 5, which shows graphically the progress of the structural changes as the cooling-temperature falls past the critical points.

This graphical statement, as well as the figures of Table III., show that structural changes occur *only during the retardations, and that they begin and end with them.* The five bars quenched above Ar_2 all have the same micro-structure, made up entirely of martensite. As soon as the retardation Ar_2 begins, however, some ferrite is set free, increasing rapidly in amount as the cooling proceeds and the retardation becomes more marked. In the middle of Ar_2 we find about 30 per cent of structurally free ferrite. Between Ar_2 and Ar_1 the metal contains some 70 per cent of ferrite and 30 of martensite. The structure then remains unaltered until the second critical point is reached. The four samples quenched between Ar_2 and Ar_1 have a similar structure. This is well shown in Fig. 5. With the beginning of Ar_1 we find another structural change taking place, i.e., the martensite begins to be replaced by ferrite; and the transformation, like the preceding one. continues as long as the retardation lasts. At the very beginning of Ar_1 we find only 1.60 per cent of pearlyte. At the end of that retardation the steel contains 22 per cent of ferrite, only 2 per cent of martensite remaining unchanged. Below Ar_1 there is no more martensite; the steel is made up of some 22 per cent of pearlyte and 77 of ferrite. The seven bars quenched below Ar_1 show that no more change of structure takes place on further cooling. The microstructural composition retained in steel by sudden cooling below the critical range does not differ from that of the slowly cooled metal.

Résumé. — *Each critical point is accompanied by a structural change which begins and ends with it. In the ranges of temperature where there is no critical point, we find no change in the microstructural composition.*

Fig. 5

Ferrite

Pearlite

Martensite

Per cent in volume

Quenching temperatures deg. cent.
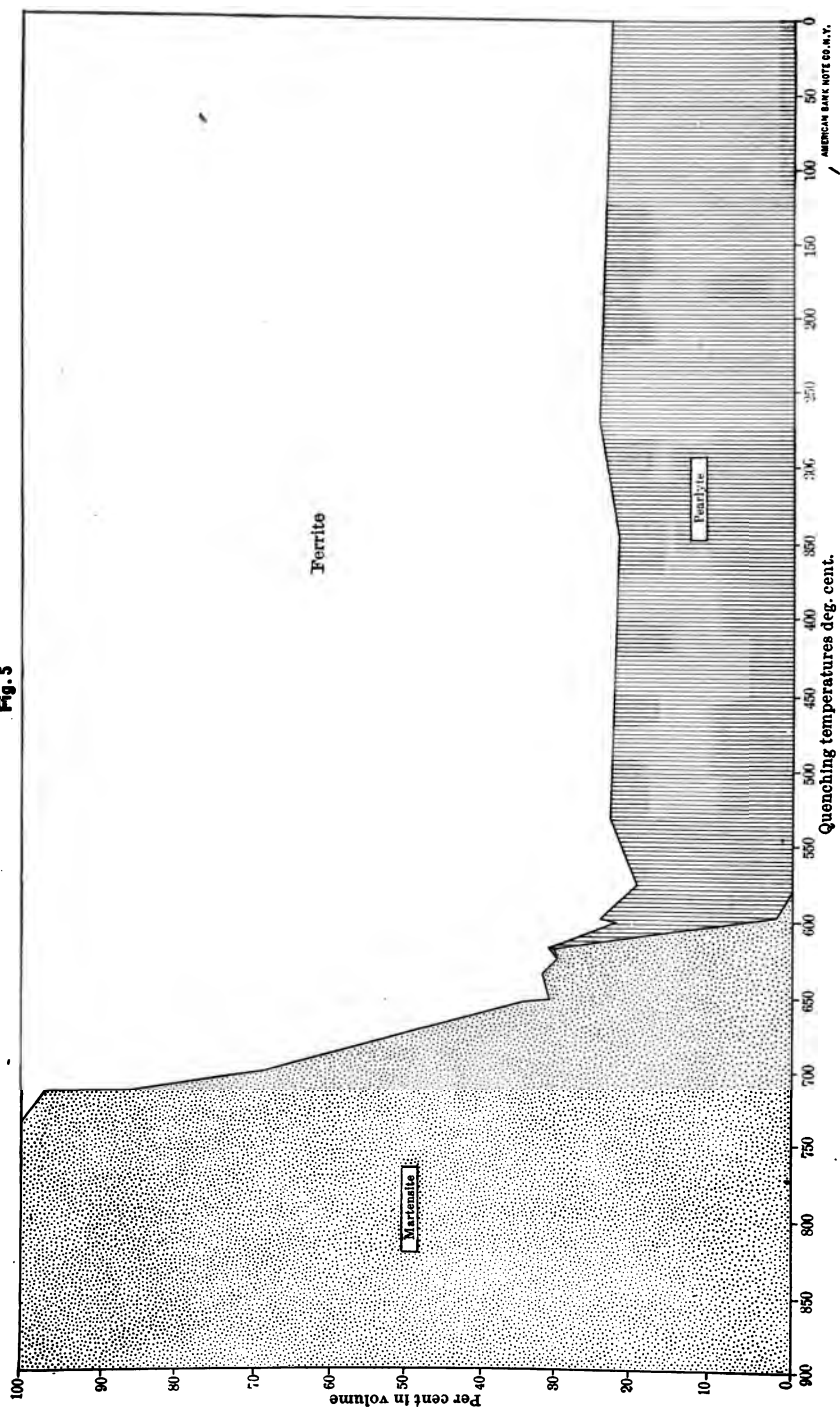
MICRO-STRUCTURAL COMPOSITION OF QUENCHED STEEL CONTAINING 0.21% CARBON

AMERICAN BANK NOTE CO. N.Y.

Assisted by the microscopical evidences presented in the first part of this paper, the writer then reviews critically the various theories which have been advanced to explain the hardening of steel.

The following presentation of the two main theories is quoted from Mr. Howe :

"Both these theories are of the *status quo* kind, i.e., each holds that the sudden cooling acts by preserving a special condition which exists at a red heat, but is unstable at lower temperatures, and does this by denying the time which is required for the change from that condition to the normal condition stable at the common temperature, and such as we find in annealed steel. At and above a certain critical range, ... the A of Osmond, ... the carbon passes spontaneously from the normal condition called 'cement-carbon,' to a special condition called 'hardening-carbon,' which below that range is unstable, tending to pass back to the cement-state, and actually so passing back during slow cooling. It may, however, be preserved by sudden cooling, and hence is found in hardened steel. While the carbon-theory regards this known preservation of carbon in the hardening-state as the direct cause of hardening, the allotropic theory holds that its action is indirect; that above the critical range, the iron passes spontaneously to a strong, hard, brittle, allotropic state called β, which, like the hardening-carbon, is unstable below that range, but which, still like the hardening-carbon, passes back relatively slowly from the β to the α state, so that the β state may be preserved by sudden cooling."

Mr. Howe himself has tried to reconcile these two opposite theories by attributing the hardening of steel to the existence at a high temperature, and the retention by sudden cooling, of a carbide of an allotropic form of iron ; and he calls his theory the "carbo-allotropic" theory.

Prof. Arnold, in a paper recently read before the British Institution of Civil Engineers, attributes the hardening of steel, not to the carbon as such, but to the existence above the critical range of a very attenuated and very hard carbide of iron. This will be here called the *subcarbide theory*.

Each theory accounts in its own way for the critical points, and attributes to the carbon and iron above, between and below the retardations such conditions as are in accordance with its claims. These facts, as well as the microscopical evidences, are summarized in Table IV.

TABLE IV.

	Carbon Theory.	Allotropic Theory.	Carbo-Allotropic Theory.	Prof. Arnold's Sub-Carbide Theory.		Microstructural Evidence.
Conditions of carbon and iron above Ar_3.	Iron and hardening-carbon.	Carbon diffused in γ iron.	Carbon diffused in γ iron.	Carbon and iron combined as $Fe_{24}C$.	?	Very mild steel, made up of martensite and ferrite.
Cause of the evolution of heat at Ar_3.	?	Passage of the iron from the γ to the β state.	Passage of the iron from the γ to the β state.	Dissociation of $Fe_{24}C$.	Formation of $Fe_{24}C$.	Separation of a certain amount of ferrite previously included in martensite.
Conditions of carbon and iron between Ar_3 and Ar_2.	Iron and hardening-carbon.	Carbon diffused in β iron.	Carbon diffused in β iron.	?	Carbon and iron combined as $Fe_{24}C$.	Soft and medium-hard steel, made up of martensite and ferrite.
Cause of the evolution of heat at Ar_2.	?	Passage of the iron from the β to the α state. Steel becomes magnetic.	Passage of the iron from the β to the α state. Steel becomes magnetic.	Passage of iron from a plastic to a crystalline condition.		Separation from the martensite of an additional amount of ferrite.
Conditions of carbon and iron between Ar_2 and Ar_1.	Iron and hardening-carbon.	Carbon diffused in α iron.	Carbon diffused in α iron.	?	Carbon and iron combined as $Fe_{24}C$.	Soft steel: martensite and ferrite. Medium-hard steel: martensite. Hard steel: martensite and cementite.
Cause of the evolution of heat at Ar_1.	Passage of carbon from hardening- to cement-state.	Carbon combining with α iron to form Fe_3C.	Carbon combining with α iron to form Fe_3C.	Carbon combined with iron to form Fe_3C.	Dissociation of $Fe_{24}C$ and formation of Fe_3C.	Disappearance of martensite and appearance of pearlyte.
Conditions of carbon and iron below Ar_1.	Iron and cement-carbon combined as Fe_3C.	Iron and cement-carbon combined as Fe_3C.	Iron and cement-carbon combined as Fe_3C.	Iron and carbon combined as Fe_3C.		Soft steel: pearlyte and ferrite. Hard steel: pearlyte and cementite.
Cause of hardening.	Retention by sudden cooling of the carbon in its hardening-state.	Retention by sudden cooling of a hard allotropic state of iron, which retention is helped by the presence of C.	Retention by sudden cooling of a hard carbide of γ or β iron.	Retention by sudden cooling of hard sub-carbide of iron, $Fe_{24}C$.	Retention by sudden cooling of a hard sub-carbide of iron, $Fe_{24}C$.	Retention of the martensite by sudden cooling.

Concluding, the writer calls attention to the importance of keeping carefully in mind the facts which have been proved beyond reasonable doubts, and which may be classified as follows:

1. Carbon-steels during cooling or heating present one or more critical points or retardation. The retardations on heating are the reversals of the corresponding retardations on cooling, i.e., one cannot take place unless the other has been induced since the former last took place. They are therefore only the opposite phases of the same phenomenon. Very mild steels have three such retardations; mild and medium-hard steels have two retardations; hard steel only one. Ac_3 and Ac_1 occur at a temperature somewhat higher than Ar_3 and Ar_1, while Ac_2 and Ar_2 nearly at the same temperature.

2. When a carbon-steel is quenched from a temperature above the critical range it is hardened in a degree roughly proportional to the amount of carbon. When quenched below the critical range it is not sensibly hardened.

3. Carbon-steel heated above the critical range is non-magnetic; below the critical range it is magnetic.

4. When hardened steel is dissolved in cold dilute acids the greatest portion of its carbon escapes as hydro-carbons. When unhardened steel is similarly treated nearly all of the carbon is found in a residue corresponding to the formula Fe_3C.

5. Each critical point is accompanied by a marked change in the microstructural composition of the metal, and no such changes occur except at the critical points.

6. Manganese-steel containing about 12 per cent of manganese does not show any marked retardation during slow cooling. It is hard and non-magnetic.

THE PRESENT CONDITION OF THE THEORIES
OF HARDENING.*

By H. LE CHATELIER.

THE theory of hardening has been, on account of its direct industrial interest, the object of a considerable number of researches, which, especially in the last decade, have been multiplied indefinitely. It is difficult to find time to keep in touch with these investigations, and if it were possible, it would be more difficult still to understand them. Too often their authors, owing to some scientific rivalry, devote their attention more particularly to the contested facts, and are led to draw the most contradictory conclusions from concordant experimental results; in order to follow the arguments, it is necessary to have taken an active part in these researches. The present résumé, in which the writer will try to be impartial, who at any rate wishes to be, will not be useless perhaps for those persons who are interested in these studies, but who have not had the opportunity to contribute to them.

Certain ferrous products (hard steel or steel which possesses the hardening power, such as tool-steels), when they are very rapidly cooled (quenched, hardened) from a sufficiently high temperature (in the vicinity of 800° or higher), acquire some properties altogether different from those which they possess after very slow cooling from the same temperature (annealed). In the hardened state their mineralogical hardness is considerably greater than in the annealed state; they scratch glass readily, and feldspar a little. Their brittleness is very great: they break under the slightest shock. That brittleness may be removed by a reheating at from 200 to 400° C. (tempering). They acquire then a high elastic limit and tenacity, which properties are utilized in the manufacture of tools, of springs, of certain parts of machinery.

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* *Revue Générale des Sciences,* January 15, 1897.

They possess a very high coercitive force for magnetism. Their electric resistance is two or three times greater than when unhardened.   Their density is reduced by 1 or 2 per cent. Finally, their thermo-electric power is considerably altered.

Those phenomena, considered collectively, characterize the normal condition brought about by hardening, what is sometimes called the "positive" hardening of steel.   In certain special cases a rapid cooling may produce different and even contrary effects, as, for instance, in the case of ferro-nickel and of manganese steel, but those are special phenomena which must be studied by themselves.

The purpose of a theory of hardening is to connect its effects with certain changes of the simple elementary factors from which depend all the properties of metals and alloys. Those elementary factors, three in number, are the following:

1. *Chemical Condition*, i.e., the nature of the elements and of their mutual combinations as they exist in the metal;

2. *Physical Condition*, i.e., the shape, dimension and distribution of the chemical constituents;

3. *Mechanical Condition*, i.e., the elastic or permanent deformation, induced in the metal through mechanical efforts; cold working produces one of the best known manifestations of such mechanical disturbances.

I. Chemical Condition.

The chemical study of the phenomenon of hardening may be divided, from a historical point of view, into three well distinct stages: the discovery of the influence of the chemical changes in the condition of the carbon; the discovery of the recalescence phenomena, which are a manifestation of these chemical changes; finally the discovery of definite carbides of iron.   It still remains to ascertain more precisely the exact part played by these carbides, and the relations which exist between their changes of condition and the allotropic transformations of the free iron, which transformations were discovered while studying the phenomenon of recalescence.

Carbon. — Carbon is the essential element of all steels which can be hardened by sudden cooling.   They usually contain from 0.2 to 1.4 per cent of that substance.   This fact,

ascertained by Karsten, Berzelius and Berthier, has been established definitively by the experiments of Marguerite and of Caron. Other foreign bodies added to iron may modify the effect of the carbon, but never replace it. All steels which truly possess the hardening power are carburetted, and, reciprocally, all irons properly carburetted may be hardened. The condition of carbon in hardened steel is different from its condition in the unhardened metal. The fact was first ascertained by Faraday. Caron, then, found that hardened steel leaves no residue upon being dissolved in warm, concentrated hydrochloric acid, while, under the same conditions, the slowly cooled metal leaves an abundant carburetted residue. Messrs. Osmond and Werth and Mr. Caron have shown that hardened steel, upon being dissolved in moderately concentrated nitric acid (Eggertz method), gives a coloration much less intense than when slowly cooled.* Weyl, Abel, Müller have isolated from unhardened steel some thin plates of a metallic carbide which are not found in the hardened metal.

There exists a relation, if not very exact, at least approximate, between the condition of the carbon and the mechanical properties of the metal.

Recalescence. — An altogether new light has been thrown upon the hardening theories by the study of the phenomena which take place when a piece of steel is slowly heated or cooled. These experiments have revealed that the phenomenon of hardening is caused by a transformation, by a reversible change of state, which is produced in steel by heating; but which disappears during cooling, if the cooling is sufficiently slow, without leaving any trace, at least of a chemical nature, of its momentary existence. The phenomenon is in direct relation with the chemical condition of the carbon, but this was not immediately recognized.

[Prof. Le Chatelier explains here the recalescence phenomenon which is described at length on page 27 and seq. of the present number of *The Metallographist.* — ED.]

Mr. Charpy's experiments have definitively established the direct correlation which exists between the recalescence phenomenon and the changes in the mechanical properties

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* See Mr. Jüptner's paper in this number of *The Metallographist.* — ED.

produced by hardening. The minimum temperature required
to produce hardening is different when that temperature is
reached by heating from what it is when it is reached by cool-
ing, since the two inverse transformations do not take place
at the same temperature [see page 28 of this journal. — ED.].
Mr. Howe illustrated this fact by showing that a piece of steel
could be hardened or not by sudden cooling from the same
temperature according as to whether the quenching-tempera-
ture was reached during cooling or during heating.

The study of the recalescence phenomenon has therefore
an important bearing upon the hardening theory; this study
has been done by Mr. Osmond through some experiments
carried on with remarkable precision, and to which sub-
sequent investigations have added but little. He has shown
that the slower the heating, the lower the temperature at
which the transformation takes place; and that the slower the
cooling, the higher the temperature of the reverse transforma-
tion, so that in the case of infinitely slow heating or cooling
the reversible transformations would occur at the same tem-
perature, probably near 710° C.*

These facts present the greatest analogy with those which
accompany all the changes of state in bodies, especially with
the allotropic transformations, of which that of sulphur may
be given as an instance. That substance presents two allo-
tropic varieties whose properties, crystalline form, density,
specific heat, heat of combustion, etc., are different. They are
called, according to their crystalline form, octahedral sulphur

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* Mr. Howe has vividly depicted the possible explanation of the
influence of the rate of cooling upon the position of the temperature of
recalescence in the following words, in which he calls V the range of tem-
perature covered by the phenomenon, Va the beginning of the recales-
cence: "Va is a fixed point, like the normal freezing-point of water; but,
just as we can cool water below its freezing-point without completely
freezing it, thereby rapidly increasing the strength with which the water
tends to freeze, so by relatively rapid cooling we can carry the metal con-
siderably below V without giving the V-change time to proceed far,
strengthening the while the tendency toward this change, which keeps
kindling more and more till it bursts into a blaze, with such evolution of
heat as actually to recalesce, to raise the temperature of the metal by some
10°, in spite of the continued abstraction of heat by the continued cooling
of the furnace." — ED.

and prismatic sulphur. The first is normally stable in the
cold for all temperatures below 95.6°; the second variety is
stable at higher temperatures. By heating octahedral sulphur
above 95.6° it is transformed with absorption of heat into pris-
matic sulphur, but not instantaneously. Its rate of trans-
formation is the greater, the higher the temperature, so that
the temperature at which the transformation takes place is
the higher, the more rapid the heating. Inversely, prismatic
sulphur cooled below 95.6° is transformed into octahedral
sulphur with a velocity which first increases as the tempera-
ture is lowered, reaching its maximum at about 60°, then
rapidly decreases, becoming very feeble at the atmospheric
temperature, and absolutely null at — 30°. Prismatic sulphur,
cooled rapidly, may reach a temperature of — 30° without
undergoing any appreciable transformation, and may then be
preserved indefinitely in the same state. In all similar cases
these phenomena follow the same course, the absolute value
of the speeds of the transformations alone varies from one case
to the other, and, therefore, also the temperature below which
the instable variety may be preserved indefinitely. In the
instance of the two varieties of oxide of lead, litharge and
massicot, the speeds of the transformation are still less than
in the case of sulphur, and the massicot, which is the variety
normally stable when hot, may be preserved at the ordinary
temperature. It is an instance of the general law which
governs the speed of all chemical phenomena. That speed is
the greater: (1) the higher the absolute temperature; (2) the
wider the range between the actual temperature and the tem-
perature of equilibrium, i.e., of reversible transformation of
the chemical system.

Above the transformation-point these two determinative
conditions vary in the same direction, and the speed increases
without limit; below, they vary in opposite direction, giving
rise, in this way, to the existence of a maximum speed.

This notion of variable speeds of transformations accounts
for all the particularities of the phenomenon of hardening; it
explains the varying temperatures at which the transformation
occurs, according to the rapidity in the changes of tempera-
tures [i.e., rate of cooling or of heating. — ED.]; it accounts
for the preservation in the cold, partially at least, through

rapid cooling, of the metal in a condition which is the one normally stable at a high temperature, and finally it explains the tempering effects produced by a subsequent elevation of temperature. The normal point of transformation in the case of steel is located at about 710° C.; above that temperature the speed of transformation increases so rapidly that it is hardly possible to raise the temperature of transformation more than 100° through a very rapid heating. During cooling, the speed reaches its maximum at about 600°; becomes very feeble below 200°, and nearly null at the ordinary temperature. The metal will be truly hardened only when it passes very rapidly through the range of temperature included between 700° and 200° C. The only object of all the formulas used in hardening consists in causing the metal to pass through the various temperatures with the proper velocity, which velocity must vary according to the final degree of hardness required. In order to produce a uniform hardness, all through the metallic mass, the law of variations of the temperatures [the rate of cooling. — ED.] would have to be identical for all the points of that mass; this is impossible, since the cooling can take place only through the outside surfaces. It is possible to approach that final aim, to a certain extent, by varying the nature of the hardening medium during the operation itself: quenching alternately in water and in air, or in water and in oil, and by modifying the effects of hardening through suitable tempering operations. It is, however, impossible to produce absolutely the desired conditions, and this explains the incredible number of hardening formulas, each one being possibly less imperfect for a certain given case. Finally, above certain dimensions, real hardening of large pieces becomes impossible, whatever the process used, because the total amount of heat to be removed increases as the cube of the dimensions, and the amount carried away in the unit of time as the square of the same dimensions. The rate of cooling decreases, therefore, with these dimensions, and eventually becomes insufficient to prevent the transformation from taking place.

While the speed of the transformation taking place during the recalescence is regulated principally by the temperature, it also depends upon its own stage of advancement; so

that at each temperature the speed, relatively great at the start, diminishes progressively, finally coming to a complete stop, at least for temperatures below 400°. This fact is utilized during tempering. A piece of steel, hardened in cold water, and then allowed to remain at the atmospheric temperature, undergoes a spontaneous tempering, very feeble, it is true, but which manifests itself by some slight deformations, and, in the case of magnets made of steel which has not been tempered, by a notable diminution of magnetism. Little by little, however, these changes become less noticeable, and in time appear to cease completely. A piece of hardened steel, upon being heated to 200°, undergoes, during the first minutes, marked changes; its electrical resistance, its hardness, its brittleness diminish; but after a few hours it seems to reach, according to the experiments of Barus and Strouhal, a state indefinitely stable, and still the tempering is far from being complete. If the same steel is heated to a little higher temperature, 300° for instance, the tempering effects are increased, and new changes of properties take place, which in turn have a certain determined limit.

Reaching this point, it seems that the chemical theory of hardening is very nearly complete. Its effect must be to prevent during cooling the recalescence transformation from taking place, to preserve the steel at the ordinary temperature, with the properties belonging to it, in that condition which is normally stable at a high temperature. It would then remain only to determine the exact nature of the carbides of iron existing in steel, and the nature of their chemical transformations taking place during the recalescence and which are prevented by sudden cooling. As soon, however, as it is tried to thus narrow down the problem, its complexity manifests itself, and its solution seems to move further away from our reach, at each step taken forward, as will be seen in reviewing our present knowledge of the carbides of iron.

Carbides. — [M. Le Chatelier describes here the four principal constituents of steel: ferrite, pearlyte, cementite, martensite (hardenite); their mode of occurrence, of distribution, etc. This subject has been treated at length on page 30 and seq., to which the reader is referred. — ED.] M. Le Chatelier continues as follows:

In spite of the absolute contradiction between the points
of view of Mr. Osmond and Mr. Arnold, the facts which they
have observed, far from being contradictory, complete each
other.   It is known that among mixtures, or mutual dissolu-
tions of two substances, there exists one, the "eutectic" alloy
("cryohydrate" of aqueous solutions), which has a certain
fixed composition, and which, on that account, has long been
taken for a definite combination.   The eutectic alloy is the one
which is saturated at the same time with the two constituents;
during cooling they crystallize together; its composition
remains invariable, and, therefore, also its point of solidifica-
tion.   Starting from a dissolution of any composition, the
constituent which is in excess is first deposited, the solution
holding a gradually increasing proportion of the other con-
stituent, until it also reaches its saturation-point.   At that
instant the composition of the remaining liquid is that of the
eutectic alloy, whose fixed point of crystallization is also the
lowest possible.

Eutectic alloys generally exhibit after solidification a
peculiar structure, resulting from the extreme minuteness of
the crystals of the two constituents, and which can be dis-
tinguished only under the highest magnifications.

Mr. Charpy* has ascertained, through some recent
experiments, that most of these eutectic alloys are made up
of extremely thin lamellæ of the two constituents; their
appearance is exactly that of pearlyte [see Frontispiece.—ED.].

It is precisely the same phenomenon which takes place
in steel.   Martensite is a solid solution of ferrite (pure iron)
and of cementite (Fe_3C), which, on cooling, always reaches
the same composition, that of *hardenite*, which is the eutectic
alloy of martensite.†   Its elementary composition is inde-

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* Mr. Charpy's paper will be published in the next number of *The
Metallographist.* — ED.

† The term "hardenite" was proposed by Mr. Howe to designate the
hard constituent of carbon-steel quenched above the recalescence-point.
Martensite, as defined by Mr. Osmond, might be considered merely as an-
other name for the same constituent.   The distinction which Mr. Le Cha-
telier makes between these two terms should be noted.   According to his
definition, hardenite contains the same amount of carbon as pearlyte, and
should occupy very nearly the same area.   In undersaturated steel (con-
taining less than, say, 0.80 per cent of C) martensite seems to reach the

pendent of the relative proportions of iron and carbon; its proportion varies only with regard to the amount of ferrite or of cementite present in the metal. If the iron, however, contains some foreign elements, such as silicon and manganese, the composition of the eutectic alloy may be altered, as is the case in ordinary dissolutions, through the addition of foreign substances. Hardenite, on crystallizing, yields pearlyte, resulting from the juxtaposition of the very minute crystals of its two constituents, ferrite and cementite; this crystallization, as in the case of liquid solutions, is accompanied by a considerable evolution of heat which gives rise to the phenomenon of recalescence.

The only difficulty with regard to this theory, and it is not a real one, comes from the fact that we are not accustomed to study solutions in the solid condition. Their existence is, nevertheless, real, and is compatible as well with the amorphous as with the crystalline state. Glass and other isomorphous mixtures, in which the proportion of the constituents may be varied at will, are real solid solutions; only the saturation-phenomena are not generally detected, because the absence, or at least the slowness, of the diffusion-phenomenon prevents the reaching of a definite system of equilibrium. Yet the tendency towards a saturation-equilibrium manifests

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composition of the eutectic alloy (i.e., becomes hardenite) when the critical point Ar_2 is passed, while in oversaturated steel hardenite is found at much higher temperature (see Plate I., page 40). While it is true that the formation of pearlyte in steel, during cooling, is strikingly suggestive of the formation of any eutectic alloy in liquid solutions, yet there is one particular in which the two phenomena differ materially, and which should not be overlooked. A piece of steel containing, say, 0.20 per cent of carbon, at a high temperature, is made up wholly of martensite, in this case an alloy of iron and carbon containing a large excess of iron with regard to the composition of the eutectic alloy. In liquid solutions the constituent which is in excess separates *gradually* and *steadily* until the eutectic composition is reached, when they both crystallize together. In the case of this iron alloy, however, the composition remains unchanged until a critical point (Ar_3) is reached, when some of the iron is separated quite suddenly during a narrow range of temperature. The composition of the remaining martensite (which is not yet that of hardenite) then remains *constant* until a second critical range (Ar_2) is reached, during which it is freed from the remaining excess of iron, and thus reaches the composition of the eutectic alloy (see page 44 and seq.; also Table III., page 46). — ED.

itself in the devitrification of glass. In the case of iron, on the contrary, the diffusion of the carbon takes place, as is shown in the cementation-process, as readily as that of salts in water, and an equilibrium of saturation is reached whenever the changes of temperature are not exceptionally rapid.

Reaching this point, it again seems as if the theory of hardening had been established; sudden cooling will prevent the splitting-up of the martensite or of its eutectic alloy, the metal retaining in the cold the condition which is normally stable at a high temperature.

This simple theory, however, is exact only in the case of certain exceptional products, such as ferro-nickel with 25 per cent Ni, and manganese steel with 13 per cent of Mn, which have none of the properties of true steels; ferro-nickel and manganese steel exhibit at the ordinary temperature the same properties which they possess, in common with all other steels, above the temperature of recalescence, i.e., a nearly complete absence of magnetic properties, a very great electric resistance and considerable malleability. Ordinary steels, on the contrary, after they are quenched, are magnetic, are not malleable, and exhibit an electric resistance, superior, it is true, to that of the same steels slowly cooled, but much inferior to the enormous resistances which they possess at a high temperature. Finally, they are in a state of internal tensions, which manifest themselves through the deformations of quenched pieces, and through their spontaneous ruptures which sometimes take place with all the violence of an explosion. They have not, therefore, preserved all the essential properties which they possessed above the recalescence.

All that may be deducted from our present knowledge of the chemical phenomena called into play by the process of hardening is, that sudden cooling prevents a *certain* number of these phenomena to take place, as it is proved by the special condition of the carbon in quenched steel, and by the evolution of heat during tempering, but that it allows certain others to occur, as is shown by the re-apparition of the magnetic properties and by the diminution of the electric resistance.

The important fact, however, discovered by Mr. Osmond while investigating the recalescence-phenomenon, namely, the existence of several allotropic transformations of the iron,

will, doubtless, permit to elucidate the points which to-day still remain obscure in the theory of hardening.

Allotropic Transformations of Iron. — The already great complexity of the phenomenon of hardening, when the part played by the iron carbides alone is considered, is much increased through the existence of several allotropic changes of the iron, the two most important of which were discovered by Mr. Osmond, and the third more recently by Messrs. Hall and Curie. The first two take place between 700° and 900° C., i.e., at the usual hardening temperatures; they may, therefore, affect that operation.

These three allotropic transformations are characterized by absorptions of latent heat during heating (Osmond), by variations of electric conductivity (Henry Le Chatelier), by a change of magnetic properties (Curie), and by variations of volume. They occur respectively at 740°, 850° and 1280° C. [see Fig. A., page 14. — ED.]. The first is especially identified with a nearly complete disparition of the magnetic properties of iron; it is accompanied by a slight absorption of latent heat, and its position varies little, being little affected by changes in the rate of cooling or of heating. It occurs, moreover, nearly at the same temperature during heating and cooling.* The second transformation is especially characterized by a sudden change in the law of variations of the electric resistance, which is then ten times greater than at atmospheric temperature, but which practically ceases to increase above this critical temperature. This transformation, like that of recalescence, is affected by the rate of cooling or of heating.

The importance of these two retardations, during heating, decreases as the carbon-content increases. The retardation taking place at 740° C. disappears completely when the metal contains more than 0.4 per cent of carbon, and that occurring at 850°, when more than 0.15 per cent of carbon is present. Moreover, micrographic analysis has shown that these proportions of carbon are precisely those corresponding

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* See also page 27 and seq., in which these transformations, or rather the temperatures at which they take place, are called critical points or retardations, and are designated respectively by the symbols Ar_1, Ar_2 and Ar_3. The first refers to the recalescence-point, the second and third to the changes occurring at about 740° and 850°, as stated by Mr. Le Chatelier. — ED.

to a total absorption of ferrite by the martensite at 740° and 850°. The retardations observed by Mr. Osmond are connected, therefore, exclusively with the changes which take place in the condition of the free ferrite.

On the other hand, my experiments concerning electrical resistances still indicate the existence of a change at 850°, even in highly carburetted steel, with this difference that the temperature at which it takes place is somewhat lowered, being near 800°. If these experiments are not erroneous, we must conclude that the iron included in the martensite undergoes an allotropic change similar to that which it undergoes in the free state, the temperature of the change alone being altered. This would be in agreement with all other analogies; the changes in the conditions of water, which manifest themselves through the existence of its maximum of density, are again met with, in aqueous solutions; but the temperature of that maximum has been displaced. The change, taking place in the martensite, may escape detection in Mr. Osmond's cooling method, if it occurs somewhat slowly; for it would not, then, give rise to any appreciable retardation. Further investigations are necessary to resolve these apparent contradictions. If it is temporarily accepted that martensite presents two allotropic transformations corresponding to those of iron, but occurring at temperatures lower than 740°, we shall be led to suppose, with Mr. Howe, that, in hardened steel, martensite, i.e., the dissolution of ferrite and of cementite, remains unaltered as a dissolution, but in a condition corresponding to the variety of iron which is stable above 740°, i.e., the magnetic variety. Quenching prevents the splitting-up of the dissolution during the recalescence-period, but it allows iron to again assume its condition normally stable in the cold. Such a partial change, taking place in a completely solid metal, induces the tensions already mentioned. In the case of ferro-nickel and manganese steel there is neither splitting-up of the martensite, nor return of the iron and nickel to their magnetic condition. This last chapter of the theory of hardening, however, is based upon experimental data too frail to be considered in any other way than as a seductive theory, deserving to be submitted to severe experimental tests.

II. Physical Condition.

It is certain, however, that the chemical transformations do not alone regulate the phenomenon of hardening. Hardened steels with the same composition and in the same chemical condition often possess very unlike properties. While, as it has been shown, there exists a dominant relation between the chemical state of carbon and the tenacity of the metal, it is nevertheless true, that decidedly different tenacities, resulting from various hardening and tempering operations, may correspond to the same carbon-condition. The cause of these variations must be looked for in the variations of the physical structure, that is, of the forms and dimensions of the elementary constituents of the metal.

Mr. Osmond has shown that in iron and steel, — and such is the case also in other metals and alloys,— the crystals nearly never exhibit the simple forms which we are accustomed to find in salts deposited from aqueous solutions. They do not form convex polyhedrons limited by plane surfaces regularly inclined over each other, but present the appearance of fern-leaves, of bearded feathers, of dendrites, what is called in petrography "crystallites," and of which the star-like crystals of snow constitute a well-known instance. During the solidification of molten metals, and as the crystallization proceeds, the branches of these crystals increase in thickness, leaving finally, between them, an empty space of varying dimensions, and in which the most fusible constituents solidify last, without any apparent outline. Such a dendritic crystal and its filling, considered as a whole, constitutes what Mr. Osmond has called a cell. These cells are broken or disaggregated by the mechanical pressure resulting from the forging or rolling; but they may, under certain conditions of temperature, be reconstituted without the metal being again melted. Quenching plays an important part in these changes of structure, by modifying the exterior form and dimensions of the cells as well as their internal constitution. The two factors influential in these structural changes are the quenching-temperature and the condition under which takes place the passage of the metal by the point of recalescence.

Quenching-temperature. — On being heated above 800° C. iron assumes sufficient malleability to permit a recrystallization to take place, which will be the more complete and the more rapid, the higher the temperature. Brinnell and Tchernoff, who have studied this phenomenon, have, however, reached different conclusions.

According to Brinnell the absolute value of the temperature to which the metal was heated intervenes alone ; according to Tchernoff, on the contrary, it is only necessary to take into account the rate of cooling from that temperature.

A high temperature, although it may be much inferior to the melting-point, has a tendency to make all metals brittle, as it has been shown by Mr. A. Le Chatelier; it increases the grain of their fracture, and deprives them of all elongation when being ruptured ; in a word, it burns them. The temperature capable of producing the totality of this effect varies according to the nature of the metal : it is located between 150° and 200° in the case of zinc, at about 900° for copper ; it decreases when the metal contains fusible impurities, and under other imperfectly determined conditions. Iron behaves similarly, it is rapidly burnt above 1000° C. Steel, which is more fusible, may be burnt above 900°. Phosphorus greatly facilitates the occurrence of the phenomenon, it accelerates it and lowers the temperature at which it takes place.

On the other hand, the rate of cooling from the maximum temperature (reached in heating) to the recalescence-point has a no less marked influence, although very different, upon the dimensions of the cells. This has been shown by the investigations of Messrs. Osmond and Sauveur, who have ascertained that the dimensions of the martensite-cells vary progressively with the temperature.* They increase in size through the absorption of the ferrite or of the cementite present in excess; and the resulting structure may be retained in the metal by rapid cooling to a temperature below the recalescence-point ; it disappears, on the contrary, during slow cool-

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* The martensite-cells, however, have not been found to vary *continuously* with the temperature. Their changes of dimensions occur only during the two upper critical points; between these points they apparently remain unaltered. See Table III., page 46, and Plate I., page 40; also footnote, page 59. — ED.

ing on account of the inverse alteration in the constitution of
martensite.   For the same carbon-condition, therefore, the
structure of the metal will vary with the quenching-tempera-
ture.   When quenched at a sufficiently high temperature, all
steels appear homogeneous, they no longer contain either
cementite or ferrite.   When quenched just above the recales-
cence-point, such homogeneity exists only in the case of the
saturated metal (containing from 0.8 to 0.9 per cent C).   These
differences of structure explain the contrary effects produced
by quenching soft and hard steels at a high temperature.
The disparition of the ferrite increases the hardness of the
former, the disparition of cementite lowers the hardness of
the latter.   These modifications of structure are not altered
by tempering ; the chemical condition of the carbon changes,
but the surfaces of the cells of pearlyte remain identical with
those of the martensite-cells from which they originate.

   Passage by the Recalescence-point. — In passing through the
recalescence-range steel again assumes a temporary mallea-
bility, which allows the metal to take new crystalline orienta-
tions.   This malleability is easily ascertained by means of the
following experiment : if a steel-bar heated to a bright-red
color be held horizontally by one of its extremities, it will
not bend as long as the temperature remains sufficiently high ;
but as soon as it reaches the recalescence-point, it will deflect
under the sole action of its weight, although being then
hardly red-hot.

   Brass presents an instance of such crystallizations cor-
responding to similar changes of state, as it has been dis-
covered by Mr. Charpy.   The metal, after having been cold
drawn, so as to efface all appearance of crystallization assumed
during solidification, takes up again a beautiful crystalliza-
tion on being reheated to about 700°, i.e., in the vicinity of a
temperature at which the metal seems to indicate, during
heating, a sudden absorption of latent heat, a characteristic
sign of changes of state.

   In the case of steel a crystallization also occurs during the
recalescence-transformation, but its nature is more complex,
and is different during heating from what it is during cooling.

   During *heating*, when steel passes by the recalescence-
point, its general structure, the forms and dimensions of the

cells are completely modified; nothing remains of the previous
structure. If the metal had previously been forged, so as to
efface all trace of crystallization due to solidification, a new
crystallization appears by reheating above the recalescence-
point, exhibiting an absolute complete cellular structure. The
metal in its cast condition is similarly affected; alternate cool-
ings and reheatings from above and below the recalescence-
point finally destroy its original structure. The large den-
dritic crystals formed during solidification are replaced by
cells which are still dendritic, but whose dimensions are
much smaller. These phenomena have been studied espe-
cially by Brinnell.

During *cooling*, on the contrary, the external shape and
dimensions of the cells are not altered during the recalescence-
transformation, their interior structure alone being modified
when the cooling has been sufficiently slow to fail to produce
any hardening, or when the hardening was followed by tem-
pering. In both cases martensite is replaced by pearlyte, i.e.,
the homogeneous structure of the cell is changed into a lami-
nated structure due to the juxtaposition of the lamellæ of
ferrite and of cementite, which constitute pearlyte. The
dimensions of the elements of pearlyte, however, vary con-
siderably according to the temperature at which it was formed.
Its structure is very minute when it has been developed by
tempering a piece of hardened steel, and it imparts then a
silky appearance to the fracture; it is much coarser when
constituted in the vicinity of the recalescence-point through a
very slow cooling. The fracture of the metal shows then a
relatively large grain, because the fracture takes place along
lamellæ sufficiently developed to extend through the whole
thickness of a cell.

In brief, the thermal treatment which must necessarily
accompany the process of hardening modifies the structure of
steel by altering the form and dimensions of its cells, as well
as their internal constitution. The passage by the point of
recalescence induces the development of a new cellular crys-
tallization which effaces all previous structure, the confuse
structure of forged steel, as well as the crystalline structure of
the cast metal, the dimensions of the cells increasing with
the temperature, partly owing to the absorption of ferrite by

the martensite, partly on account of a special crystallization which takes place in all metals heated to a plastic condition, and leading towards the so-called *burnt* state. The first of these increments of the cells' dimensions disappears during slow cooling, and can be retained only through a sudden cooling which denies the cells of martensite the necessary time for their retrogradation to the hardenite-condition; the second increment, on the contrary, is permanently acquired. It can only be made to disappear through a subsequent special treatment of the metal, such as remelting, forging, or repeated reheatings past the point of recalescence.

These various changes in the cellular structure play an important part in metallurgical operations. In order to remove the natural brittleness of cast steels, they are heated a certain number of times past the recalescence-point, either through proper reheatings, or by means of successive quenchings. It is possible, in this way, to increase the elongation originally less than 5 per cent to 20 per cent and over. Moreover, by quenching and tempering steel of medium hardness, a more homogeneous metal is obtained, which may then be forged or drawn in the cold more easily than the same metal slowly cooled. The latter has a heterogeneous structure, being constituted by the juxtaposition of cells of pearlyte and of ferrite of inequal hardness. The former, on the contrary, is made up exclusively of a pearlyte as homogeneous as the martensite from which it originates, and whose hardness is intermediate between that of ordinary pearlyte (the pearlyte derived from hardenite) and that of ferrite.*

The so-called "negative" hardenings, resulting from

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* The distinction which Mr. Le Chatelier makes between the pearlyte of tempered steel and the normal pearlyte, described at length on page 33, should be noted. Accepting the author's meaning of the term hardenite, the pearlyte of slowly cooled steel originates from the transformation *in situ* of the cells of *hardenite* into cells of pearlyte. It has a constant composition (see page 34). The pearlyte of tempered steel, on the other hand, is derived from the transformation *in situ* of the cells of *martensite* into pearlyte. Its composition, therefore, may vary, since that of martensite varies. It is, however, *only* in relatively soft steel (containing less than 0.40 per cent of C), quenched at a high temperature, that the martensite differs in composition from hardenite. *Only* in that case, therefore, can the tempering pearlyte be different from the normal pearlyte. — ED.

quenching in warm bath, such as molten lead, or even in oil ·
in the case of thick pieces, do not produce a real harden-
ing; they are equivalent to a hardening immediately followed
by a tempering, and their action is to render the metal homo-
geneous.

The special crystallization resulting from too high a
reheating, on the contrary, is always injurious; it increases
the final brittleness of the metal, whether it be quenched or
slowly cooled. It is necessary, therefore, when hardening, to
avoid heating the metal to a higher temperature and for a
longer time, than is strictly required. Such is also the case
in connection with any operation evolving the reheating of
the metal. When forging or rolling, for instance, the crystal-
lization destroyed by the mechanical kneading is again spon-
taneously reconstituted, if the operation is finished at too
high a temperature, and the cooling too slow. It is difficult
to finish the work at a low temperature (in the vicinity of
$600°$ or $700°$ C.); as it would be desirable, because the rigidity
of the metal at that temperature would necessitate an exag-
gerated expenditure of motive force; but the forged pieces
may be rapidly brought to the desired temperature by the use
of water in sufficient quantity to produce a kind of negative
hardening, which will fix the structure resulting from the
forging or rolling, but will allow the recalescence to take
place.

While the thermal treatments affect especially the out-
side dimensions of the cells, it must be borne in mind that
they may, as it has been seen, affect at the same time their
internal constitution. The influence of negative hardening
on the elongation, certainly caused partly by the greater
homogeneity of the metal, must also be related to the greater
fineness of the grain of the fracture, resulting from the
greater tenacity of the constituents of pearlyte, which in this
case was constituted more rapidly and at a lower temperature
in a less malleable metal.

Double Quenching. — To complete this subject, a few
words should be said concerning double quenching (*double
trempe*). This operation consists in quenching the metal a
first time, reheating it to $600°$ C. (i.e., below the recalescence-
point), and then quenching it again. This treatment dimin-

ishes considerably the brittleness of the metal by suppressing
the sudden occurrence of a marked permanent set (indicated
by a jog in the strain-diagram), which is usually developed
in testing the annealed metal.   The method, first proposed
by Mr. Walrand, and applied since to various parts in ord-
nance-work, was carefully studied by Mr. A. Le Chatelier,
and his results led to its systematic use in the navy depart-
ment for certain parts of machinery.   It is certain that this
special method does not call into play any chemical action,
the metal being chemically in the same condition as when
annealed.   It is probable, therefore, that changes of structure
alone are called into play.   A few photomicrographs published
by Mr. Martens seem to confirm this view, but no systematic
study has yet been made of this question.

III. Mechanical Condition.

The properties of all metals are temporarily or perma-
nently modified when they are subjected to mechanical efforts
capable of producing elastic or permanent distortions.   Hard-
ened steels are under enormous internal stresses ; it is, there-
fore, necessary to take into account the possible influence of
these efforts upon the properties of the metals.

It is quite certain that the origin of these tensions is to
be found in the variations of volume which accompany the
transformation of iron from its non-magnetic to its magnetic
condition, because ferro-nickel or manganese steel, which
retain the non-magnetic state, are not subjected to such
internal stresses.

Metals which have undergone permanent distortions,
which are what is called "cold-worked" (*écroués*), possess
some properties which make them similar in many ways to
quenched steel.   Their elastic limit is considerably increased,
their malleability very low, and annealing causes the dis-
appearance of these characteristics just as in the case of hard-
ened steel.   These analogies were described long ago by
Tresca.

Mr. Osmond, in comparing cold-worked and annealed
steel, observed that cold-working does not, like hardening,
change the chemical condition of the carbon, but that it

increases, however, as does hardening, the heat of dissolution of the metal in acids. These facts led him to infer that the effects, caused by hardening and by cold-working, were due, in part, to the existence of the same allotropic variety of iron produced by these two distinct operations. But this hypothesis, which was not supported by any direct evidence, appears now to be abandoned.

Mr. André Le Chatelier, on the contrary, considering the cold-worked state as a property common to all metals, and characterized in every case by an increase of hardness, but independent of all allotropic transformation proper, proposes the following explanation to account partly for the increase of the elastic limit of soft steels, which increase seems altogether out of proportion with the amount of iron-carbides present in such metals : he would attribute it to the cold-working (*écrouissage*) to which the free iron must necessarily be subjected, during cooling, when it undergoes its allotropic transformation with change of volume in a solid metal, whose form remains unaltered, partly on account of the cooling of the exterior surface, partly through the existence of an internal unyielding net-work of carbide.

As a matter of fact, with the exception of the existence of a direct influence of the internal stresses on the properties of hardened steel, and which must be added to the influences of the changes of chemical condition and of physical structure, nothing has been conclusively established concerning this point.

Summing up, hardened steel is a homogeneous mixture, a solid dissolution of a carbide of iron (Fe_3C) and of the magnetic variety of iron, which dissolution is, as in the case of glass, in a state of supersaturation, and may, like glass, split up at a sufficiently high temperature into its two elementary constituents. But, unlike glass, hardened steel is not amorphous : its structure is more like that of crystalline isomorphous mixtures.

The dimensions and forms of the crystallized elements, of the cells, which have a great influence upon the properties of steel, depend principally on the treatment to which the metal has been subjected in order to reach its actual condition.

CARBON AND IRON.*

IN this paper the author, MR. ERNEST HENRY SANITER, hoping that they may in some small degree assist in bringing to a conclusion some of the vexed points in the relation of carbon to iron, records the results of some experiments along the following lines: —

(1) The thermal treatment of Fe_8C,

(2) The saturation-point of iron with carbon by fusion in contact with excess of carbon,

(3) The saturation-point of iron with carbon by heating without fusion in contact with excess of carbon,

(4) The etching of pure carbon-iron alloys at a red heat, in order to ascertain their structure by means of the microscope at that temperature.

Thermal Treatment of Fe_3C. — About 20 grammes of Fe_8C were prepared from a " cement-bar," made from Wigan "Pure Quality" steel, containing 1.0 per cent of carbon. The carbide was prepared by the modification of Binks and Weyl's method described by Arnold and Reed. The yield of Fe_8C obtained was 14.0 per cent as against a theoretically possible yield of 14.5 per cent.

It was observed, on boiling a portion of the Fe_8C thus prepared with nitric acid of 1.20 specific gravity, that the coarser portion, i.e., that obtained from the cementite veins, was comparatively insoluble as compared with the fine flakes obtained from the pearly constituent.

An experiment was therefore made to ascertain if this peculiarity might be utilized to estimate quantitatively the cementite, and further to ascertain if the cementite thus separated had the same composition as the Fe_8C obtained from the pearly constituent.

A weighed portion of the Fe_8C was boiled for twenty minutes in 1.20 specific gravity nitric acid. The insoluble

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* Iron and Steel Institute, August meeting, 1897.

portion was then washed by decantation, dried with alcohol and ether, and weighed.

Assuming that the carbon in the original bar, exceeding 0.89 per cent, would exist as veins of cementite,† the Fe_3C prepared from the bar (1.0 per cent carbon) should contain 11.0 per cent of cementite; the amount actually found was 9.8 per cent, which had the following composition:—

	Per Cent.
Carbon	7.23
Iron	89.90
Not accounted for	2.87
	100.00

The cementite separated was of a bronze color and was evidently partially decomposed, as was shown by the deficiency in the analysis. This experiment is favorable to the supposition that the Fe_3C from the cementite and pearlyte have the same composition.

In the following table are given the results of the thermal treatment of Fe_3C under varying conditions:—

Treatment of the Normal Carbide.	Total Carbon Per Cent.	Graphitic C Per Cent.	Combined C (by difference).
Untreated	6.92	0.19	5.94*
Heated to about 1000° C., chilled in cold water.	6.13	0.56	5.57
Heated to about 800° C. in nitrogen.	6.12	0.40	5.72
Heated to about 1000° C. in nitrogen.	6.13	2.50	3.63
Fused in magnesia in CO	4.27	3.05	1.22

* Allowance made for carbon hydrate.

† This assumption contains a slight error, for while it is true that in the case of steel containing very little other impurity, pearlyte contains very nearly 0.89 per cent of carbon, it does not follow that 0.89 per cent of the total carbon goes to form pearlyte, for then the steel would be saturated, and there would be no room left for any free cementite. (See Plate I., page 40.) One per cent of carbon yields very nearly 15 per cent of Fe_3C,

The composition of the steel used and of the carbide residue were as follows: —

	Wigan "Pure" Cement-bar.	Normal Carbide Fe₃C
Silicon . . .	Trace . .	. . .
Silica . . .	Nil . .	0.09
Phosphorus . .	0.008 . .	0.004
Sulphur . . .	0.014 . .	. . .
Manganese . .	0.16 . .	0.15

It is interesting to note that the impurities found in the cement-bar are also in the Fe_3C prepared from it, in practically the same proportions, thus showing that these impurities are disseminated equally throughout the Fe_3C and the ferrite.* It is noteworthy that when the carbide was heated to 800° and slowly cooled, or when heated to 1000° and chilled, very little graphitic carbon was liberated, while upon being heated to 1000° and cooled slowly much graphite is formed, and when fused at about 1400°, most graphite is separated.

After these experiments were completed, the author discovered that a somewhat similar investigation had been carried out on Fe_3C by Mylius, Foerster and Schöne.† These investigators state that heating to a red heat does not alter it, which differ from the present experiments. They also melted the carbide, and obtained a button containing 4.36 per cent carbon, as against 4.27 in the author's experiments.

Saturation-point of Iron with Carbon by Fusion in Contact with Excess of Carbon. — This saturation-point has been the subject of various investigations in the past, amongst which may be mentioned that of Karsten, who says that iron can combine with 5.95 per cent of carbon. Percy, however, doubts

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leaving 85 per cent of carbonless iron in the steel. This iron (ferrite) unites with a certain amount of the carbide, to form pearlyte, as follows (on the assumption that pearlyte contains 0.89 per cent of C): —

$$\text{Fe} \quad \text{Fe}_3\text{C} \quad \text{Fe}$$
$$86.65 : 13.35 = 85 : x,$$

which gives nearly 13 per cent of the carbide Fe_3C absorbed by the ferrite, leaving 2 per cent as free cementite, or about 13.3 per cent of Mr. Saniter's residue, instead of 11 per cent. — ED.

* This would seem to be true only in the case of manganese. — ED.

† Messrs. Mylius, Foerster and Schöne's investigations will be described in the next number of *The Metallographist.* — ED.

this, and the author agrees with him; Riley, who found 4.0 per cent of carbon as the saturation-point; and, finally, Hochstätter, who found 4.63 per cent of graphitic carbon, with 95.13 per cent of iron, leaving 0.24 per cent unaccounted for, a considerable part of which was no doubt silicon, as the peroxide of iron and carbon used were admittedly not quite pure.

In view of these varying and doubtful results, it seemed desirable to redetermine this saturation-point. The author's endeavor was to produce a carbide entirely free from silicon. In this, even when using the greatest precautions, he was not entirely successful, as the following table will show: —

	Stead's Pure Wire used	No. 1. Wire melted	No. 2. Grey Portion of No. 1 remelted	No. 3. No. 2 remelted
Kept in molten condition hours	. . .	3	4¼	5¾
Fracture . . .	. . .	grey with white center	grey with white center	all grey
Manganese } Copper }	. Trace	. . .	. . .	. . .
Phosphorus . .	0.014	. . .	. . .	. . .
Sulphur . . .	0.011	Nil	Nil	0.005
Silicon . . .	Trace	0.024	0.04 '	0.07
Total carbon .	Trace	4.03	4.81	4.73
Graphitic carbon	. . .	3.00	3.84	4.03
Combined carbon (by difference) }	. . .	1.03	0.97	0.70

It is observable that even a few hundredths per cent of silicon has a marked effect in increasing the formation of graphitic carbon in saturated carbon-iron compounds, and it yet remains to be proved whether iron saturated with carbon, and quite free from silicon, could liberate graphite. It may, however, be taken for granted that 0.04 per cent silicon (Exp. 2) will not reduce the saturation-point of iron for carbon by much, and therefore that 4.81 per cent is not far off the truth.

Several of the buttons, including No. 2 (4.81 per cent carbon), were white in the center with grey outside. The white portion did not shade off gradually into mottled and then grey, the division being sharp, so that the grey portion could be cut and filed away from the white, as was done in

the case of No. 2 button, the separate portions being tested
for carbon as follows : —

	White.	Grey.
Total carbon	3.83	4.06
Graphitic carbon . . .	Nil	3.50

The proportion was about 1 of white to 6 of grey.

The microscopic examination of No. 3 button showed the
white portion to consist of pearlyte and cementite, while the
grey consisted of pearlyte, graphite and ferrite.

*The Saturation-point of Iron with Carbon by Heating with-
out Fusion in Contact with Excess of Carbon.* — This experiment
was made to ascertain how much carbon could be taken up
by pure iron without melting it, and to ascertain if the
amount taken up was in molecular proportion to the iron.

Very pure iron wire, 0.04 inches in diameter, was heated
to about 900° C. for varying periods in a porcelain tube full of
charcoal, at successive stages the tube was allowed to
cool, and a portion of the wire removed for analysis. The
following table shows the results : —

	Pure Iron Wire	Same after seven hours' heating	Same after fourteen hours' heating	Same after twenty-one hours' heating
Manganese, silicon, copper	Trace	. . .	. . .	. . .
Total carbon .	Trace	1.64	2.79	2.95
Graphitic carbon . . .	. . .	. . .	. . .	0.53
Combined carbon (by difference) . . .	. . .	. . .	. . .	2.42
Sulphur . . .	0.011	. . .	. . .	. . .
Phosphorus .	0.014	. . .	. . .	. . .

As only 0.16 per cent of carbon was absorbed in the last
seven hours, it was concluded that the saturation-point had
been reached at 2.95 per cent, of which amount 0.53 per cent
was in the graphitic state.

Wire of the first and second period, the microscope
showed to consist of pearlyte with bands of cementite extend-
ing in all directions from side to side. The wire after the
third heating, while consisting of pearlyte, cementite and

graphite (which last I was unable to detect with the microscope), showed a segregation of the cementite toward the center, none of the bands extending to the outside, thus showing a tendency to form a white nucleus similar to that found in the buttons produced by fusion described under another head. The outside of the wire was coated with graphite, which was carefully removed before the analyses were made.

The Etching of Pure Carbon-iron Alloys at a Red Heat, in order to ascertain their Structure at that Temperature, by means of the Microscope. — In considering this, the most interesting part of his subject, it occurred to the author, that if steel could be etched at a bright-red heat so as to show the distribution of the carbon, it would throw valuable light on the controversy which has now raged for some years on the hardening of steel.

What was required was a compound readily fusible at a red heat, which would have a selective action in attacking iron and carbide of iron at that temperature. In considering what might be suitable he was naturally led to think of calcium chloride. On trying this re-agent he was able to observe, with the naked eye, that the cementite veins were eaten away much more readily than the mass of the metal.

The piece of steel is polished in the usual manner. Calcium chloride is fused in a platinum crucible over a blast blow-pipe. When the fused chloride has reached a bright-red heat the piece of steel is dropped in and immersed by shaking.

The crucible is kept at a bright red till the piece of steel attains that temperature; after a further fifteen seconds' heating, the crucible is rapidly cooled by dipping the bottom into cold water. The steel is then rapidly dissolved out with water and dried in alcohol.

A series of pure steels with ascending quantities of carbon were etched by this method. On examining them, magnified to 250 diameters, a most interesting structure was revealed, a structure which is closely identified with the percentage of carbon present. Photomicrographs of the five steels selected and containing respectively 1.8, 1, 0.60, 0.43 and 0.10 per cent of carbon, are reproduced in the paper.

The two first samples exhibit a very characteristic struct-

ure, which appears to consist of acicular crystals, which show a marked tendency to form triangles..

The sample containing 0.6 per cent carbon shows this acicular structure strongly, while in that with 0.43 per cent carbon it is only faintly marked, and in that with 0.1 per cent carbon it is entirely absent.

These acicular crystals are, in the author's opinion, an indication of a definite carbide of iron existing in steel at a bright-red heat; and if, in accord with present theory on the subject, the carbon is retained to a large extent by chilling, in the form in which it exists in steel at a bright-red heat, it follows, as a natural corollary, that these acicular crystals are the hardening-carbide in steel.

Osmond, who, in examining that microscopic appearance of varying composition, known as martensite [page 35.—ED.], and lately alluded to in one of its forms by Sauveur as "diluted martensite," has discovered triangular shapes which he describes as "triangular crystallites of iron," presumably allotropic iron. These triangles appear to be the connecting feature between martensite and the acicular structure at a red heat, and are, no doubt, the triangles formed by the acicular crystals. This naturally leads to consider how the allotropic theory stands towards this method of investigation.

This theory assumes the formation of a hard allotropic modification of iron at a bright-red heat, which is retained in that form by chilling when there is sufficient carbon present, it being assumed that the carbon acts as a brake to retain the iron in its hard or β-condition. Of course this hard condition of iron is also assumed to exist in carbonless iron at a bright-red heat.

Before proceeding further, it seems desirable to emphasize the fact that the structure exhibited in the plates was deeply etched upon the steel at a bright-red heat; this and the subsequent rapid chilling prevents doubt as to the structure being other than that at a bright-red heat.

Now, if the acicular structure obtained by etching with fused calcium chloride were an indication of the "adamantine allotropic modification of iron," it would be equally evident with 0.1 per cent carbon as with 1.8 per cent carbon, but it is entirely absent.

We therefore come to the point that at a bright-red heat iron containing 1.0 per cent carbon has a totally different structure from iron containing 0.1 per cent carbon, and that this difference of structure is due to the carbon *per se*.

Likewise in chilled steel we have a great difference in physical characteristics between 1.0 and 0.10 per cent carbon, which cannot exist without the difference in carbon.

This method of investigation, while it gives no indication of an allotropic modification of iron, gives strong evidence that 0.6 per cent carbon or upwards causes, at a bright-red heat, a radical change in the structure of iron, which must be considered as evidence in favor of the hardening of steel being due to an attenuated carbide of iron of great hardness.*

The author concludes his paper with some considerations regarding the molecular ratio of carbon to iron found in the various stages of his experiments.

CARBON-CONDITION AND HARDENING OF STEEL.

UNDER the above title, PROFESSOR A. LEDEBUR contributes an article to *Stahl und Eisen* of June 1, 1897, opening his remarks with the following quotations: —

"Iron is a very porous metal, consisting of salts of vitriol, sulphur and earth, badly combined and mixed with each other," said, in the year 1697, the then well-known chemist Nicolas L'Emery in the fifth part of his *Cours de Chymie*.

"Steel is nobler than iron, and exists in two forms, namely, as made steel and as native steel. . . . When it is well cleaned, then heated, and quenched three or four times in equal parts of extract of radishes and water which had contained earth-worms, it cuts iron like lead." This statement was made in 1557 by the well-known naturalist and mathematician Cardanus, who gave various other fine rules for the harden-

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* These conclusions of Mr. Saniter were opposed by Mr. Sauveur in some remarks contributed to the discussion of the present paper, and which will appear in the *Journal of the Iron and Steel Institute* for 1897 (No. II.). They will be published in the next number of *The Metallographist*. — ED.

ing as well as for the softening of steel, some of which may
be found in the *Geschichte des Eisens* by Ludwig Becks.

There is a wide gap between these statements and the
truth, continues Professor Ledebur. We believe, now, to per-
ceive the goal in the distance, but it has not yet been reached.
It may be well to make a halt here, in order to glance at what
has been achieved. A special reason for this looking back-
ward is to be found in the various papers and essays on carbon-
condition and hardening, published during the last month.

A theory of hardening based on facts could only be
developed after it had been discovered that the carbon of
hardened steel exists in a form different from that of the
carbon of the unhardened metal ; or rather, only after that
variety of carbon which was considered as single and which
was called combined carbon (in order to distinguish it from
graphite), was found to exist in two different forms, which
may be present in widely varying proportions in the same
steel, after it has been hardened or slowly cooled. The first
investigations of this kind were made by Karsten in 1824, but
at first little attention was given to his discovery. Caron,
Rinman and others confirmed, and added to, the observation
of Karsten, and in 1885 Abel, in dissolving steel in a dilute
solution of bichromate of potassium and sulphuric acid, suc-
ceeded in isolating from the mass of the iron, in the shape of a
carbide, that variety of carbon, most abundant in unhardened
steel, and present only in slight traces in the hardened metal.
It is the second variety of the combined carbon. The first
variety was called hardening-carbon. Abel found the com-
position of this carbide to answer the formula Fe_3C, and
Müller, using another method, came to the same conclusion.
Rinman, who had observed earlier the presence of this carbon
in cemented steel, called it cement-carbon ; the denomination
used by Abel and Müller, however, that of " carbide-carbon,"
is more appropriate.

Whether this newly discovered carbide was a true chem-
ical compound with the above formula, or whether it was
only a solution, an alloy of iron and carbon, remained a long
time undecided, because its chemical composition showed im-
portant variations. The recent investigations of Mylius,
Foerster and Schöne have finally decided the question in

favor of the chemical combination Fe₃C, by showing clearly why previous investigators had obtained somewhat varying results.*

That this carbide-carbon is the one which colors the nitric acid solution of the Eggertz method, and that such determination, therefore, can only be accurate when both the standard and the steel to be compared were slowly cooled, had already been clearly shown by Osmond.

Professor Ledebur describes briefly the recalescence-phenomena and the carbon-theory of hardening, already explained on page 49, concluding that further researches may be expected to strengthen this probable theory. He then relates the discovery, by Osmond, of the upper retardation of soft steel (see page 27 and seq.), stating that from the existence of these critical points and from the fact that the tenacity of iron, containing very little carbon, can be very greatly increased by sudden cooling, the allotropic theory of hardening was developed.

Professor Ledebur then describes Mr. Howe's† experiments dealing with the hardening of nearly pure iron by sudden cooling, and concludes with the following remarks:—

Is the established fact that nearly carbonless iron assumes different properties, when suddenly cooled, from those which it possesses after slow cooling from the same temperature, a proof of allotropy? If the question is answered in the affirmative, then such must also be the case with copper, bronze and other metals and alloys, for they, too, exhibit variations in their properties when quenched and slowly cooled. Changes of properties, corresponding also to changes of structure, are doubtless produced by different rates of cooling; but a change very similar to that due to quenching is also produced by cold working, and, like the former, is also removed by subsequent reheating. If it is accepted that there are two allotropic varieties of iron, it would not necessarily follow, as Osmond contends, that the cause of hardening in the true sense is to be found in the retention of the hard allotropic

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* The investigations of Messrs. Mylius, Foerster and Schöne will be described in the next number of *The Metallographist.* — ED.

† These experiments will be described in the next number of *The Metallographist.* — ED.

form, and that carbon plays only an accessory part. The author then describes the occurrence and distribution of martensite as set forth at length on page 44 and seq., and concludes by saying that among all the theories of the phenomenon of hardening which, in recent time, have been based on microscopical investigation, that which attributes the hardening-effect of quenching to the retention of martensite in the cold metal, is the simplest and easiest to understand.

MICROSCOPE ACCESSORIES FOR METALLOGRAPHERS.

IN this short paper, read by Mr. J. E. Stead at the May meeting (1897) of the Iron and Steel Institute, the author describes some appliances destined to facilitate the work of the metal-microscopist.

FIG. 1. Wrought Iron showing Cinder.   FIG. 2. Carbide of Iron in Blister Steel.

The most interesting part of his paper, however, will be found in his description of a method for ascertaining the weakest portion of the sample under examination.

It is often desirable, says Mr. Stead, after the examination of a metal, to determine what part of the structure is weakest, and this we have found can often be determined by

bending the microscopic section itself, either by steadily applied pressure, or by percussive force, taking care of course to arrange to have the polished surface convex. This can be readily effected by placing the section, polished side down, over a V-space cut out of a solid piece of steel, and applying force to the back so as to bend the specimen.

Sometimes a piece breaks, but that does not matter; for the two portions are then placed together again in a glass slide, and are examined, when the track of the fracture can be readily traced, and the nature of the structure through which it has passed noted.

If the piece does not break right through, the weak places often do give way, and it is easy to see under the microscope what the structure is like at these places.

The diagrams illustrate fully the value of this method of investigation.

Fig. 1 is a piece of wrought iron which has been bent in a line with the grain, or ·direction of rolling, showing the weakness located where the cinder is present.

Fig. 2 shows that the cementite or carbide of iron in blister steel is the track along which the fracture travels.

NEW TYPE OF MICROSCOPE FOR THE EXAMINATION OF OPAQUE BODIES.*

By H. LE CHATELIER.

THE accompanying sketch shows a new type of microscope for metallographic studies, and was constructed, according to my instructions, by Mr. Pellin. The inverted position of the stage facilitates the arrangement of the fragments of metal which may then, with the exception of the polished surface, be of any shape.

The horizontal pencil of light received by the illuminating prism D is refracted upwards and taken up by that half of the objective which is covered by the prism D. The two faces of the prism make an angle of 45°, one of them forming

an angle of 22.5° with a horizontal line, the other a similar
angle with a vertical line, which causes the axis of the re-
flected pencil to be vertical. The extreme edge of the prism
intersects the axis of the objective, and also its principal focus,
or, at least, comes as near doing it as possible. The dia-
phragm E, placed at the conjugate focus of the object exam-
ined, and the screen F with its rectangular opening, provide
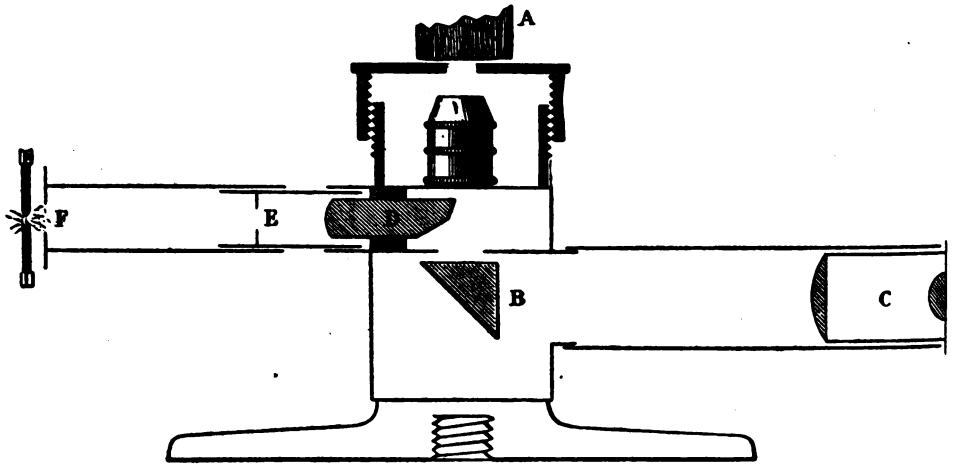
Microscope for the Examination of Opaque Bodies.

A, object being examined; B, total reflexion-prism directed towards the
   eye-piece C; D, illuminating-prism 10 mm. in side dimension and
   30 mm. long, made up at one end by two total reflexion-faces forming
   an angle of 45°, and at the other end by a lens with a principal focal
   length equal to the length of the prism, i.e., 30 mm.; E, diaphragm
   placed at the conjugate focus of the object with regard to the optical
   system composed of the objective and the prism D; F, movable ver-
   tical screen placed at the conjugate focus of the first lens of the
   objective with regard to the prism D; the illuminating-flame is
   placed in front of F.

a means for cutting off all the useless rays, whose diffusion
by the lenses of the objective would otherwise illuminate the
field of the microscope, and diminish the visibility of the
images. To reach this result, the diaphragm E must have an
opening exactly equal to the diameter of the image of the use-
ful portion of the object under examination; and the opening
of the screen F, a height equal to half the dimensions of the
image of the upper lens of the objective.

NOTES AND COMMENTS.

The International Laboratory of Zurich, Switzerland. — Professor Wedding's report of the proceedings of the Stockholm Congress of the International Association for the Testing of Materials, to which he was sent, as a special delegate, by the German Association for the Promotion of Industry, gives an interesting account of that successful meeting. He devotes his attention, more particularly, to the chemical testing of iron and steel. After recalling that it was in Zurich, in 1895, that the importance of adopting uniform methods for the analysis of iron and steel was first vigorously brought forward and the first steps taken in that direction, Professor Wedding relates the failure of their efforts to interest in the work a sufficient number of noted chemists from all metallurgical countries. In the majority of cases they obtained only promises of co-operation which never materialized. It was then decided to create an international laboratory whose main purpose would be to investigate systematically and exhaustively all the methods now in use for the analysis of iron and steel, and to decide upon standard methods to be used in all countries, just as standard test-pieces are used for physical testing. This would not, by any means, stand as an impediment to the progress and development of chemical methods, for whenever a better method is devised, it would, after proper investigation, be quickly adopted and the old one discarded.

Zurich was selected as the most desirable location for the new laboratory, because being situated in a so-called international country it could not give rise to any national jealousy. Having no iron-works of importance, the objection that the Laboratory was destined to benefit its iron industry at the detriment of that of other countries could not be raised. Zurich has a university and a polytechnic school, and the necessary room and equipment to carry on its work is very courteously placed at the disposal of the International Laboratory.

The next step was, to find a competent person to take charge of the Laboratory. The question was happily solved when it was found that Baron Jüptner von Jonstorff, the well-known and accomplished chief chemist of the great Austrian iron-works of Neuberg, was willing to assume these duties.

It then remained to secure the money needed, — 30,000 marks a year, — a very small sum to be contributed by all the iron-works and technical associations of the world.　The first efforts, however, met with little success, but finally a sufficient number of steel-works responded, especially in Germany, England, Austria, Sweden and Belgium, and now the existence of the International Laboratory is an accomplished fact.

Many works are still hesitating, but, says Professor Wedding, when it is made clear that the work of this Laboratory will benefit them, they will, I believe, co-operate with those already enlisted.　What is beneficial to the iron industry in general, must necessarily be beneficial to the individual iron-works.

The Lavoisier Medal of the French Society of Encouragement for the National Industry, which is destined to those authors, of any nationality, whose works have most contributed to the progress of French industry, was presented last July to Mr. F. Osmond for his metallographic researches.

Mr. Jordan, in enumerating the titles of Mr. Osmond to this award, reviews at length the work accomplished by the distinguished metallographist.　The results of his investigations have proved of great value in the treatment of steel, throwing a very beneficial light upon those important questions of heat-treatment which, although solved in part by the brilliant memoirs of Tchernoff, remained yet in many particulars so imperfectly understood. Ordnance officers especially appreciate and acknowledge the services rendered by Mr. Osmond through this better understanding of the nature and behavior of steel.　His discovery of the upper retardations of soft and medium-hard steel, an almost irrefutable evidence of allotropy, stands as one of his most brilliant and valuable achievements.

The influence of Mr. Osmond's researches, moreover, has acted as a stimulus in inducing others to seek for metallurgical improvement in this newly opened field, resulting in an activity which must necessarily lead to the advancement of both the art and the science of metallurgy.　This is the third prize which the Society of Encouragement awards to Mr. Osmond, the first having been presented to him in 1888, the second in 1895.
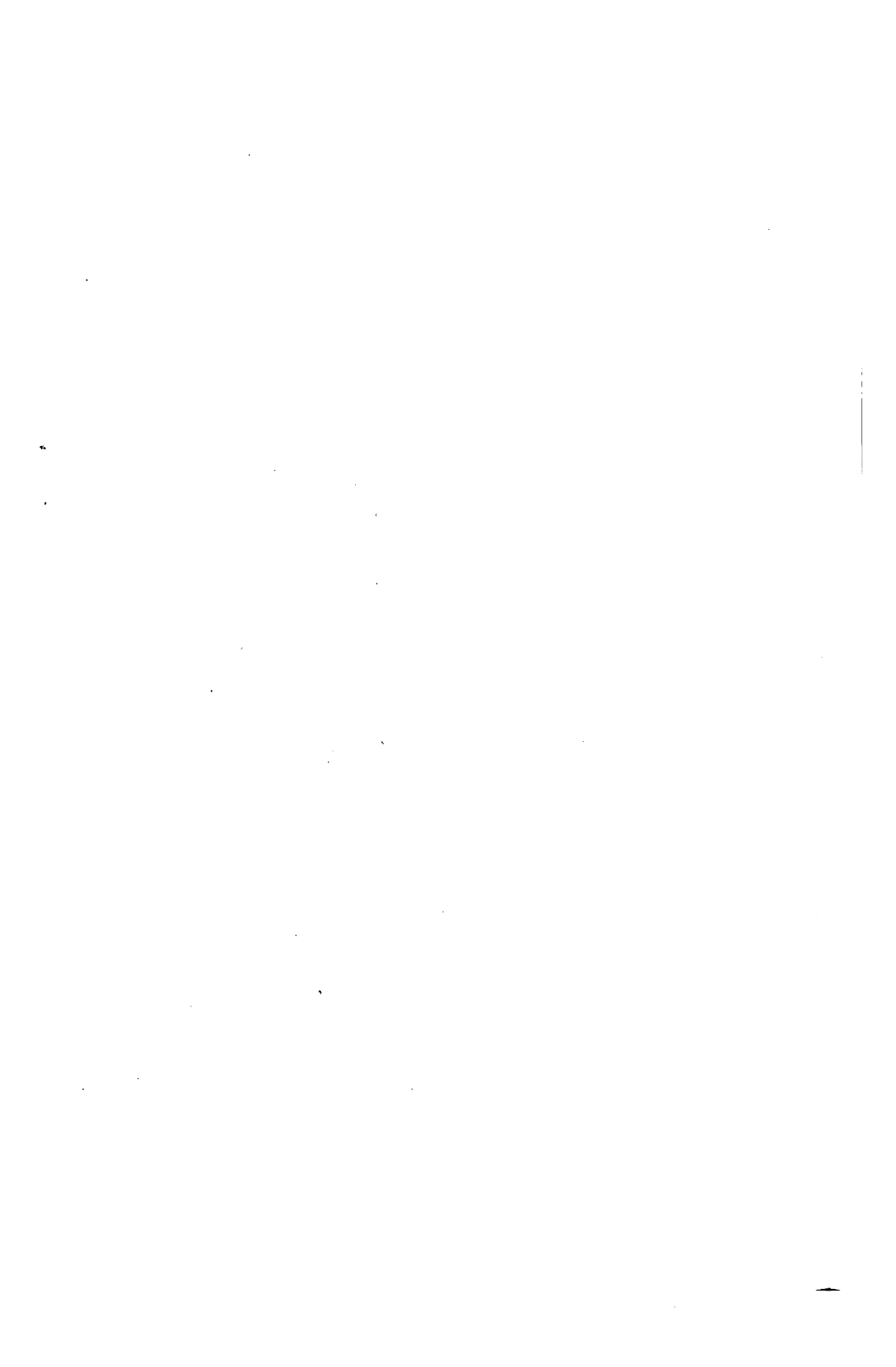
FIG. 1.   Eutectic Alloy of Tin and Bismuth.
Magnified 200 diameters.
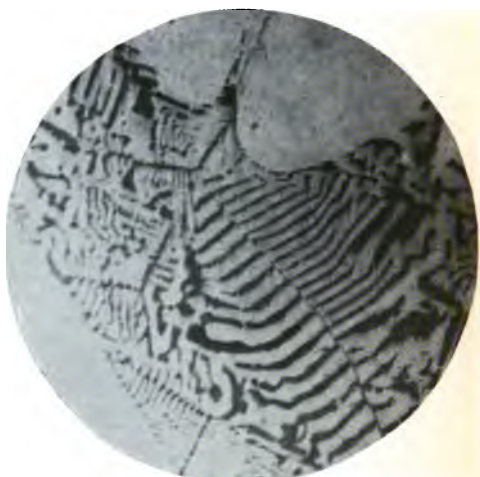
FIG. 2.   Alloy of Silver and Antimony.
Ag 66 per cent — Sb 34 per cent.
Magnified 200 diameters.

FIG. 3.   Alloy of Copper and Antimony.
Cu 65 per cent — Sb 35 per cent.
Magnified 100 diameters.
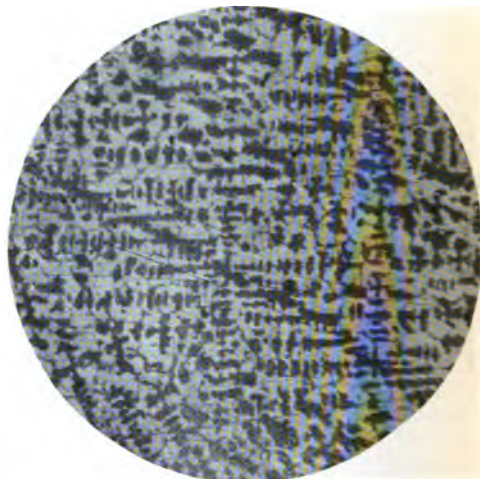
FIG. 4.   Alloy of Copper and Antimony.
Cu 85 per cent — Sb 15 per cent.
Magnified 30 diameters.

PHOTOMICROGRAPHS OF METALS, after CHARPY.

MICROSCOPIC STUDY OF METALLIC ALLOYS.*

By G. CHARPY.

THE microscopic study of metals has until now been applied more especially. to industrial alloys. These researches have led to important results in the department of technical metallurgy, but they imply few general deductions concerning the constitution of alloys. This is due to the fact that the metals which are of industrial use are those whose structures are most complicated. Alloys which are composed of two metals simply in close contact possess naturally properties which differ little from those of the metals, and so they were empirically left aside in order to utilize the alloys whose complex constitution renders it possible to obtain properties superior to those of the component metals.

On account of this complexity, industrial alloys are not well suited to furnish indications regarding the constitution of metallic alloys; with that end in view, it is preferable to start from alloys having a constitution as simple as possible, and to approach gradually the most complicated cases. The researches described in this memoir have been conducted accordingly; we have taken as guide previous studies deal-

* Bulletin Société. d'Encouragement pour l'Industrie Nationale, March, 1897.

ing with the physical properties of alloys and especially those dealing with the curve of solidity, and which have been communicated to Mr. H. Le Chatelier in a series of articles,[*] and to Mr. H. Gautier.[†]

1. Technology.

The samples to be examined through the microscope are first filed or ground on an emery-wheel, then rubbed on emery papers of increasing fineness, and finally polished upon a very fine piece of chamois leather, using first some brilliant rouge, and then a very small quantity of very fine jewelers' rouge.

The polishing of hard metals presents no great difficulties, but such is not the case for soft alloys, especially if they contain a large proportion of lead or tin: it is then impossible to obtain a specular polish, the soft metal spreading, very much like a fat substance, over the whole surface of the preparation. With care and patience, however, it is possible to produce surfaces upon which a proper chemical action outlines the structure with distinctness.

Polishing alone sometimes suffices to render visible the hardest constituents or those which are colored, but a chemical attack is generally required. While it is indispensable, when studying a certain alloy for the purpose of ascertaining the transformations produced by a certain mechanical or thermal treatment, to employ a well-defined and always identical etching method, such is not the case when it is desired to characterize the various constituents of alloys; on the contrary, it is useful then to use successively different re-agents, the comparison of the results obtained in this way being one of the best means of ascertaining the nature of a certain constituent.

The re-agents most frequently used are the various acids, caustic potash, ammonia, and alkaline sulphides; they are used in the shape of very diluted alcoholic solutions, in order to destroy the action of fatty substances which sometimes remain on the surface of the preparation. The specimens are

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* *Bulletin Société d'Encouragement*, February, April, and May, 1895.
† *Idem*, October, 1896.

placed upon a platinum plate, thus giving rise to the formation of an electric couple, which greatly regularize the chemical action.

It is often possible to render the structure apparent by heating the metal in contact with the atmosphere; the various constituents are then oxidized successively and assume different colorations. As gaseous re-agent, hydrosulphuric acid should be noted; it gives good results with certain silver alloys.

Finally, the method most generally used consists in etching the preparation by electrolysis, by placing it in a saline solution and connecting it with the positive pole of a battery whose negative pole is connected with a platinum plate or wire.

[Mr. Charpy states here that the preparation must generally be examined by direct reflected light, i.e., by light reflected downwards along the axis of the microscope, and explains some of the appliances employed for obtaining such an illumination. They will be described exhaustively in an early number of *The Metallographist.* As a source of light, the writer used an incandescent lamp, and his objectives were Nachet's instruments. He also recommends the use of projection eye-pieces for photographic work. — ED.]

Microscopic examinations do not always permit to ascertain conclusively the nature of the various constituents which are revealed, but they furnish indications which, considered jointly with the properties of the same substances, would lead almost to a certainty.

The various constituents hardly ever occurring as well-formed crystals, but as *crystallites* with curved and ill-defined edges, the shape of the constituents can only give, in general, roughly qualitative indications.

The relative hardness of the various constituents furnishes one of the best means of distinguishing them; polishing upon a somewhat thick piece of chamois leather suffices generally to cause the hardest components to stand in relief; hard crystals are found even in alloys composed of soft metals; they are then unquestionably made up of a definite compound; such is the case for alloys of copper and tin, of silver and tin, etc.

Mr. Behrens has, in some instances, measured the relative hardness of two adjacent constituents by scratching them with needles made up of metals of known hardness.

The color of the constituents often furnishes useful information ; a violet compound is found in alloys of antimony and copper ; in alloys made up of copper and zinc, or of copper and tin, those parts which contain much copper are yellow, while those containing much zinc or tin are white, etc.

The method most generally applicable consists in studying the action of different re-agents upon the various microscopic constituents. In the case of lead and tin alloys, for instance, hydrochloric acid covers the crystals of lead with a white layer of chloride of lead, while it dissolves the tin ; nitric acid, on the other hand, dissolves the lead and covers the tin with a white layer of metastannic acid. In the case of silver alloys, hydrosulphuric acid imparts a black coloration to those parts which contain most silver ; when copper alloys are treated with ammonia, the areas rich in copper are oxidized first.

Finally, attention should be called to a somewhat unexpected method of investigation, which has been indicated for the first time by Mr. Albert Sauveur and applied to steel, i.e., the use of the planimeter.* It furnishes a means of measuring the areas occupied by the various constituents, thus giving, so to speak, a proximate analysis whose results, compared with those of ultimate analysis, afford valuable information. We have applied this method in several instances, and in the case of alloys of antimony and silver it has revealed the probable existence of a definite compound, because of the considerable gap existing between the calculated proportions of the various constituents and those actually observed.

Planimetric measurements are evidently only approximate ; they suppose the alloy to be quite homogeneous, and, on that account, can better be applied to industrial metals than to alloys prepared in small quantities, for experimental purposes, and cast under conditions which generally allow segregation to take place ; these measurements, however, are

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* See *The Metallographist*, Vol. I. No. 1 (January, 1898), page 39 and seq., for a short description of the use of the planimeter in micrographic work. — ED.

none the less very important; besides the information concerning the relative proportion of the various constituents, they give a means of expressing, in a precise manner, the dimension of the grain, which seems to be the best characteristic of the conditions in which solidification has been effected.

II. Eutectic Alloys.*

The constitution of *eutectic* alloys, or alloys with the *lowest melting-point*, was one of the most interesting questions to be studied through microscopic examination. The property to melt at a temperature lower than all other mixtures of the same substances has long been considered as a characteristic of a definite compound. This preconceived idea seems even to have led certain investigators to accept inaccurate results concerning the composition of those alloys. So it is that Rudberg indicates that the most fusible alloy of tin and bismuth corresponds to the formula Sn_3Bi_2, which melts at 143° C., while, as a matter of fact, according to Guthrie, the most fusible alloy melts at 133° and contains 46.1 per cent of bismuth instead of 45.74 per cent required by the formula Sn_3Bi_2.

The fact that the composition of eutectic alloys cannot, in general, be expressed by simple multiples of atomic weights has been conclusively established by Dr. Guthrie in a series of memoirs published in the *Philosophical Magazine* from 1875 to 1884. We shall quote here a few passages of his last article, entitled: "On Eutexia" (*Philosophical Magazine*, June, 1884) :

". . . The eutectic alloys of metals, many of which have been long imperfectly known, and the eutectic alloys of salts, which I shall describe, are the perfect homologues of the cryohydrates.

"The statement, therefore, that alloys of minimum melting-points are got on mixing the metals in certain simple ratios of their atomic weights is presumably to be put on one side. As the cryohydrate forms itself when a salt-solution of any strength loses heat, so the eutectic alloy forms itself when an alloy whose constituents are in any ratio is cooled.

* See Professor Roberts-Austen's lecture on alloys in the present number of *The Metallographist*. Also Vol. I. No. 1 (January, 1898), page 19 and seq., Mr. Osmond on eutectic alloys; and page 59 and seq., Mr. H. Le Chatelier on the same subject. — ED.

"That certain metals may and do unite with one another in the small multiples of their combining weights may be conceded. To such bodies the eutectic alloys bear the same relationship as the cryohydrates bear to the common hydrates, and, like the latter bodies, their constituents are not in the ratio of any simple multiples of their chemical equivalents. But their composition is not, on that account, the less fixed, nor are their properties the less definite.

"Firstly, as a salt may unite with water, as when anhydrous chloride of calcium does so, to fix the water as crystalline water, and also may unite with water as a cryohydrate, so two metals may unite in one proportion while they form a definite eutectic in another. Secondly, the very bodies resulting from the chemical union of the two metals will possibly, and probably, furnish starting-points of new series of eutectic alloys, consisting of a simple metal on the one hand, and the chemical alloy on the other."

We are therefore led, when two metals may be mixed in all proportions, to consider some of these alloys as more especially definite. Some of them are true chemical combinations, being formed with evolution of heat through the union of simple multiples of atomic weights; others, which constitute the portions solidifying last when an alloy is allowed to cool, have a constant composition, but which cannot generally be expressed by a simple formula. The latter may be compared to those solutions which distillate with a constant composition (such as mixtures of hydrochloric acid and water, of alcohol and water, etc.), which phenomenon, as shown by Mr. Berthelot, does not in any way imply the existence of a definite compound.

What, then, is the composition of these eutectic mixtures? Are they chemical combinations of a peculiar character or homogeneous mixtures, sorts of solid solutions which might be compared to glass; or else, are they heterogeneous mixtures in which the two substances exist in close contact in an extreme state of division? Various researches have been undertaken in order to elucidate this question. Mr. Offer has shown in 1880 that the cryohydrates, i.e., the mixtures of aqueous saline solutions, never form well-defined and transparent crystals, but opaque masses; that alcohol dissolves the ice and leaves a crystalline net-work of solid salt; that the heat of dissolution is equal to the sum of the heats of dissolution of the ice and of the salt; finally, that the specific weight is equal to the mean specific weight of the constituents.

By means of colored salts or by utilizing the phenomena of polarization, Mr. Ponsot ascertained, in 1895, that the cryohydrates were made up of juxtaposited crystals alternately of ice and of solid salt, the latter anhydrous or hydrated.

These experiments seem to demonstrate clearly that the eutectic mixtures are heterogeneous mixtures.

The microscopic study of the eutectic alloys of metals has given us results identical to those of Mr. Ponsot regarding the cryohydrates. The eutectic alloy of tin and bismuth was first examined. 200 grammes of the alloy was prepared by melting together some tin and some bismuth in the proportions indicated by Mr. Guthrie, i.e., 46.1 per cent of bismuth and 53.9 per cent of tin. It was allowed to cool slowly from the molten condition; when most of it had solidified, the portion remaining liquid, and which possessed exactly the composition of the eutectic alloy, was decanted. This portion, after solidifying, was the one used for the study of the structure.

The examination of a polished surface, etched with very dilute hydrochloric acid which dissolves the tin only, shows that the two metals are simply juxtaposited; the crystals are extremely minute, requiring relatively large magnifications to be clearly distinguished. Fig. 1 (Frontispiece) shows a photomicrograph of one of these preparations magnified 200 diameters; the black portions indicate the bismuth, the white areas the tin which was dug out by the acid. This figure is a negative of the true appearance of the preparation, it having been found that, in this case, a negative print was better suited to reproduction. It is seen that some portions of the surface are made up of white grains, while others reveal a striated structure in black and white. This appearance is produced only when the solidification has taken place very slowly; if the metal be suddenly cooled, the whole surface is uniformly striated, but the crystals are then so small that it is very difficult to obtain satisfactory photographs. It would seem that during slow cooling a first separation takes place of portions rich in bismuth and of portions rich in tin, the metals separating subsequently in each of these portions in the shape of thin plates or lamellæ. In the parts appearing white in the photograph there are indeed very fine

brilliant striæ which have nearly disappeared in the repro-
duction. This very finely laminated structure seems to be
characteristic of eutectic alloys. We have found it in every
case which has been examined; it is always perfectly distinct
in the portions of alloys solidifying last, and surrounding
crystals of some pure metal or of some definite compound.

Fig. 2 (Frontispiece) shows an alloy containing 66 per
cent of silver and 34 per cent of antimony, magnified 500
diameters; the preparation has been treated with hydro-
sulphuric acid, which darkens the silver while it has no action
on the antimony. This figure was also reproduced from a
negative print, so that here the silver appears white. The
alloy is made up of large areas of silver surrounded by the
eutectic alloy which clearly exhibits the alternate layers of
silver and antimony.

Instances of such splitting up of eutectic alloys will not be
multiplied here, as we shall meet them repeatedly farther on.

Eutectic alloys, therefore, whose composition is perfectly
known, exist in the solid state as simple mixtures of their
constituents. The very minute division of these components
is sufficient to impart to them special properties; it may be
conceived, for instance, why in a number of cases they exhibit
a conchoidal fracture, which would lead, at first sight, to con-
sider them as homogeneous bodies.

We have found the same characteristics in the mixtures
of melted salts, which may be ground down to very thin
plates, one or two tenths of a millimeter in thickness, and
then examined as transparent objects. In most cases, trans-
parent crystals are detected, surrounded by a mixture which
is relatively opaque, owing to the refraction-phenomena pro-
duced by the very tenuous crystals of which it is composed.
These small crystals may be distinguished, under high mag-
nifications, in the thinnest portions of the preparation.

III. Alloys with Normal Curves of Fusibility.

According to Mr. H. Le Chatelier, the normal curves of
fusibility of binary mixtures may be grouped according to
three types: (1) two branches of curves starting from the
melting-points of the pure metals and meeting at a point cor-

responding to the eutectic alloy; this curve is obtained when the two metals form neither definite combinations, nor isomorphous mixtures; (2) three branches of curves, two of them starting from the melting-points of the pure metals, and a third exhibiting a maximum and crossing the former two in two points corresponding to two eutectic alloys; it is the case of two metals forming a definite combination; (3) the curve of fusibility is continuous and unites the melting-points of the two metals; it is the case of two metals forming isomorphous mixtures.

Alloys whose curves of fusibility corresponded exactly to the three normal types were first examined, namely:

In the *first group*, alloys of tin and bismuth, of lead and antimony, of lead and tin, of zinc and aluminium.

In the *second group*, alloys of copper and antimony, of nickel and tin.

In the *third group*, alloys of bismuth and antimony.

Alloys of Lead and Antimony. — The curve of fusibility, determined by Mr. Roland-Gosselin, is composed of two branches meeting at a sharp angle and corresponding to the alloy containing 13 per cent of antimony, from which it is inferred that the metals are merely in close contact. Mr. Laurie, on the other hand, finds that the electro-motive forces of these alloys vary in a continuous manner with the composition, which would lead to suppose that the metals crystallize together.

The microscopical examination clearly confirms the inference drawn from the curve of fusibility.

In the case of alloys containing 13 per cent of antimony, hard crystals of antimony are found, surrounded by a eutectic alloy whose splitting up becomes visible after a weak attack with nitric acid. Figs. 5, 6 and 7 exhibit the appearance, magnified 200 diameters, of alloys containing respectively about 70, 40 and 20 per cent of antimony, and photographed after having been polished and without further treatment.

Alloys containing from 0 to 13 per cent of antimony present an entirely different aspect; they are difficult to polish, but large dendrites are easily detected, which blacken when the surface is treated with sulphuretted hydrogen; they are soluble in nitric acid and are surrounded by a eutectic alloy.

The proportion of these dendrites, probably composed of pure lead, varies as the amount of lead present. The appearance of such alloys is entirely similar to that of Fig. 8.

It seems evident, therefore, that when an alloy containing less than 13 per cent of antimony is allowed to cool slowly, as soon as the beginning of solidification is reached, crystallites of lead are formed resembling fern-leaves which gradually grow as the temperature falls; when the portion remaining liquid has reached the composition corresponding to the eutectic alloy, it solidifies in bulk, the lead and the antimony

FIG. 5.   Alloy of Lead and Antimony.
70 per cent antimony.
Magnified 200 diameters.

FIG. 6.   Alloy of Lead and Antimony.
40 per cent antimony.
Magnified 200 diameters.

being then deposited simultaneously as very thin crystallitic plates. When an alloy containing more than 13 per cent of antimony is slowly cooled, a similar phenomenon takes place, but it is then the antimony which solidifies until the remaining liquid has reached the composition of the eutectic alloy.

Alloys of Lead and Tin, of Zinc and Aluminium. — The fusibility-curves of these alloys are also made up of two branches meeting at points corresponding respectively to the alloys containing lead 35 per cent, tin 65 per cent, and aluminium 5 per cent, zinc 95 per cent.

The microscopical examination yields results similar to those indicated in the case of lead and antimony. As all the constituent metals are relatively soft, the polishing operation is difficult and does not place in relief any of the components.

In the case of alloys of lead and tin, hydrochloric acid dissolves the tin while the lead is covered with a white layer of chloride. Nitric acid, on the contrary, dissolves the lead and covers the tin with a layer of white metastannic acid. The appearance of the preparation is therefore the reverse, when treated with hydrochloric acid, from what it is when

FIG. 7.   Alloy of Lead and Antimony.
20 per cent antimony.   Magnified 200 diameters.

etched with nitric acid. It is not possible to prepare a surface that will permit the use of high magnifications, and the latter are required to resolve the eutectic alloy.

In the case of zinc and aluminium, a somewhat diluted solution of caustic potash leaves the zinc nearly unaffected while it rapidly dissolves the aluminium, producing cavities which appear black under the microscope. The zinc is present in the form of radiating crystals, often as six-pointed stars in alloys containing little zinc; aluminium crystallizes in dendritic needles.

Alloys of Tin and Bismuth. — These alloys belong to the
same group and are better adapted to photographic reproduc-
tion. The structure of the eutectic alloy of these metals has
been shown in Fig. 1 (Frontispiece). Figs. 8 and 9 exhibit
the appearance of mixtures containing respectively about 20
and 60 per cent of bismuth, etched with hydrochloric acid.
In the first instance, the eutectic alloy, whose laminated
structure may be distinguished, surrounds dendrites of tin
which have been dug out by the acid and appear black ; in
the second case the eutectic alloy surrounds some white
crystals of antimony which were already discernible after
polishing.

Alloys of Iron and Carbon. — The microstructure of alloys
of iron and carbon — especially of steel — has been the object
of numerous researches, ever since Dr. Sorby created micro-
scopic metallography by applying it to the study of these
metals. It may be interesting, nevertheless, to compare
some of the acquired facts with those that we have just
described.

When the most recent researches, those of Messrs. Osmond,
Arnold and Sauveur, are compared, it is seen that they prac-
tically agree concerning the nature of the constituents of
steel in its normal condition, i.e., cooled from a high tempera-
ture sufficiently slow to allow the various transformations of
iron and carbon to take place in their integrality. Three
constituents are then found, if we omit the graphite, which
appears only under special conditions, and the forms of transi-
tion which, strictly speaking, are not constituents ; they are :*

 1. *Ferrite*, composed of nearly pure iron.

 2. *Cementite*, a carbide of iron corresponding to the for-
mula Fe_8C.

 3. *Pearlyte*, a constituent answering to the formula
$Fe_{24}C$, i.e., containing 0.89 per cent of carbon, but which
under the microscope is seen to be made up of plates, alter-
nately of ferrite and cementite.†

* The microstructure of steel has been described at length in Vol. I.
No. 1 of *The Metallographist* (January, 1898), page 19 and seq., and page 30
and seq. — ED.
 † See Frontispiece *loc. cit.* — ED.

When the steel contains less than 0.89 per cent of carbon, it is formed of ferrite and pearlyte; when it contains more than that amount of carbon, it is formed of pearlyte and cementite.*

When it is noticed that the structure of pearlyte is identical to that of eutectic alloys, being like them made up of alternate layers of two different constituents, the analogy between the constitution of steel and that of alloys like those of tin and bismuth, for instance, appears striking; steel is

FIG. 8.   Alloy of Tin and Bismuth.
20 per cent bismuth.

FIG. 9.   Alloy of Tin and Bismuth.
60 per cent bismuth.

composed of iron and the carbide Fe_3C, just as the latter alloys are composed of tin and bismuth, pearlyte correspond-

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* When the metal is made up entirely of pearlyte, it is said to be saturated. Professor Arnold found that in the case of steel containing *very little* impurities the saturation-point corresponds to 0.89 per cent of carbon — that such, therefore, is the carbon-content of pearlyte.   In commercial steel, however, containing about 1 per cent of impurities besides carbon, 0.80 per cent of carbon is sufficient to saturate it.   The pearlyte of commercial steel of that grade, then, contains in the neighborhood of 0.80 per cent of carbon, and may contain much less carbon, in the case of a more impure metal, especially if considerable manganese be present. See *loc. cit.*, page 33 and seq. — ED.

ing to the eutectic alloy. The only conclusion I wish to draw from the above considerations is that there is no reason to consider the alloy containing 0.89 per cent of carbon as a definite compound, as was recently proposed by Prof. Arnold. All the.properties invoked for that purpose are to be found in alloys formed of simple mixtures when the eutectic alloy is reached ; to the latter correspond critical points in all the properties, but, as we have seen, it does not by any means follow that this is a definite compound.

Alloys of Antimony and Copper. — The curve of fusibility of these alloys, determined by Mr. H. Le Chatelier, is composed of three branches crossing each other at two points corresponding to the alloys containing respectively about 25 and 71 per cent of copper ; the intermediate branch exhibits a maximum at about 60. per cent of copper. This leads to admit the existence of a definite compound answering to the formula $SbCu_2$, for which composition the electric conductivity, ascertained by Mr. Mathiessen, also reaches a maximum.

The microscopical examination confirms the existence of this compound, and shows that these copper alloys may be classified in four very distinct groups.

The *first group* includes alloys containing from 0 to 25 per cent of copper. After polishing, hard crystals of antimony are seen, surrounded by a eutectic alloy. The structure is distinctly revealed through an etching with diluted hydrochloric acid. Fig. 10 shows the appearance of the structure of an alloy containing 10 per cent of copper and magnified 60 diameters. The white portions are made up of crystals of antimony ; the eutectic alloy appears entirely black, because the etching was somewhat prolonged. A high magnification, however, reveals the presence of two juxtaposited elements. As the proportion of antimony increases from 0 to 25 per cent, the crystals of antimony decrease gradually, without, however, any alteration in their forms, precisely as in the case of alloys of lead and antimony described in the foregoing pages.

The *second group* includes alloys containing from 25 to 60 per cent of copper, which, upon being examined after polishing, are seen to be made up of crystallites of a distinct violet color, surrounded by a eutectic alloy appearing nearly white,

when moderately magnified, and which splits up into two
elements, especially when the preparation has been etched
with hydrochloric acid and heated in the atmosphere, so as to
induce a slight oxidation.   The violet-colored crystallites
increase in quantity as the amount of copper increases, form-
ing the totality of the alloy when the latter contains 60 per
cent of copper.   These alloys cannot be easily photographed
for want of sharpness on the sensitive film between the violet
color of the crystal and the white color of the matrix.   Fig. 11
shows the structure of an alloy containing 40 per cent of

FIG 10.   Alloy of Copper and Antimony.
10 per cent copper.
Magnified 60 diameters.

FIG. 11.   Alloy of Copper and Antimony.
40 per cent copper.
Magnified 60 diameters.

copper and magnified 60 diameters, after an etching of suffi-
cient duration to cause the crystallites to stand in relief; they
are indicated by the white areas in the reproduction.   The
composite structure of the surrounding eutectic alloy may be
detected under a moderate enlargement.

The *third group* includes alloys containing from 60 to 70
per cent of copper.   Their polished surfaces exhibit a uniform
violet tint, but under the microscope, violet-colored crystalline
grains are detected, surrounded by a net-work of a white sub-
stance made up of small crystals which sometimes penetrate

into the interior of the grains. When the metal is heated, the substance forming the net-work is oxidized first. Fig. 10 shows the appearance of an alloy containing 65 per cent of copper, magnified 100 diameters. The lighter portions correspond to the violet grains ; a few fragments of the substance which composed the net-work, and which corresponds probably to the second eutectic alloy, may be detected in the interior of the grains. Such structure, made up of crystalline grains, is met with quite frequently in alloys, notably in alloys of copper and aluminium containing 10 per cent of aluminium, in alloys of copper and tin with 25 per cent of tin, of copper and zinc with 50 per cent of zinc. Their structure is similar to that shown in Fig. 3 (Frontispiece).

The *fourth group* includes alloys containing over 70 per cent of copper. Polishing alone does not reveal their structure, but upon being heated some crystallites are first oxidized which appear to be surrounded by a eutectic alloy. These crystallites unite to form long dendritic threads which are the closer together, the larger the amount of copper present. Fig. 4 (Frontispiece) exhibits the appearance of the structure of an alloy containing 85 per cent of copper and magnified 30 diameters. The dark areas sharply outlined are probably made up of pure copper, the light portions corresponding to the eutectic alloy.

From the above considerations the constitution of alloys of copper and antimony may be explained as follows : in the case of alloys containing less than 25 per cent of copper, pure crystals of antimony are separated when solidification begins, increasing gradually in size as the temperature decreases ; the portion remaining liquid, therefore, gradually becomes richer in copper until the composition of the eutectic alloy is reached ; it then solidifies, at a constant temperature, through a simultaneous crystallization of antimony and $SbCu_2$. In the case of alloys containing from 25 to 60 per cent of copper, a similar phenomenon occurs, only it is the definite compound $SbCu_2$ which separates from the molten mass as soon as the freezing-point is reached. When from 60 to 70 per cent of copper is present, the same compound is separated, but is in this case surrounded by a second eutectic alloy made up of copper and the compound $SbCu_2$. Finally, when more than

70 per cent of copper is present, a portion of the latter is first deposited when solidification sets in, until the portion remaining liquid has reached the composition of the second eutectic alloy.*

This very simple conception results from the appearance of the curve of fusibility determined by Mr. Le Chatelier, and it is wholly confirmed by the microscopical evidences.

Alloys of Nickel and Tin. — The curve of fusibility of these alloys and their microstructure indicate that they have a constitution similar to that of the alloys of copper and antimony. The eutectic alloys contain respectively 2 and 60 per cent of nickel. A maximum occurs in the curve corresponding to about 43 per cent of nickel. An alloy containing 5 per cent of nickel exhibits after polishing a few white crystalline needles which are hard and stand in relief on a white background. The proportion of this hard substance increases with the percentage of nickel present in the alloy. With 25 per cent of nickel the needles are united, forming a continuous

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* The structural composition of alloys of copper and antimony as described by Mr. Charpy is very plainly illustrated in the accompanying diagram in which the abscissas represent the ultimate composition of the alloy, the ordinates its structural composition. The constitution of any alloy forming one or more eutectic mixtures may be illustrated in a similar way.

Copper per cent.
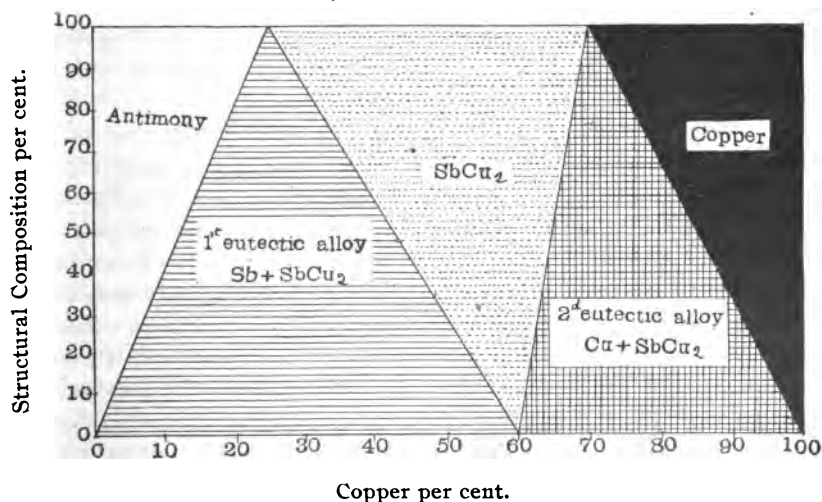
net-work.   These crystals are seen more distinctly after etching the polished surface with diluted nitric acid.   .

With 35 per cent of nickel in the alloy,·it is made up nearly exclusively of this hard constituent; it exhibits some creeks which are intensified by a nitric-acid treatment.

The structure of an alloy with 50 per cent of nickel cannot be distinguished after polishing; upon being etched with hydrochloric acid, a matrix, present only in small quantity, is dug out, placing in relief numerous crystallites with rounded and sharply defined edges.   The appearance of the alloy is similar to that of Fig. 4 (Frontispiece).   It is probably made up of the hard component surrounded by a eutectic alloy also very hard.

The alloy with 90 per cent of nickel exhibits after oxidation produced by heat, or better still, after submitting it to electrolysis in nitric acid, long dendritic needles.

These results indicate that the alloys of nickel and tin have a constitution similar to that of the alloys of copper and antimony.   The great hardness of the definite compound explains why the presence of small quantities of tin increases so much the hardness of nickel.   The hardness of the alloy appears to reach a maximum when about 40 per cent of nickel is present, which corresponds to the region of the curves of fusibility exhibiting a maximum, and also to a nearly homogeneous microstructure.   [The alloy is then made up entirely of the definite compound. — ED.]   The formula of this definite compound cannot be deducted from the microscopical evidence.

When the composition of an alloy is nearly that of a definite compound, it always possesses a nearly homogeneous structure; it also exhibits a tendency to produce crevices, owing probably to the fact that the whole mass solidifies at a temperature nearly constant, and to the absence of a more fusible constituent to fill the spaces existing between the crystals first formed.   It is difficult to distinguish these crevices from cavities which might be filled with a constituent differing from the matrix, and, on that account, the structure of the metal does not appear to undergo any sudden modification on either side of the composition which corresponds to that of the definite compound.   The microscopical examina-

tions of these alloys, therefore, as well as the study of their physical properties, point to the existence of a definite compound in a certain region, but, in order to ascertain its exact composition, it will be best to endeavor to isolate it by the use of suitable re-agents.

Alloys of Bismuth and Antimony. — These alloys are the only ones, among those we have examined, which correspond completely to isomorphous mixtures. The curve of fusibility, ascertained by Mr. Roland-Gosselin, is composed of a single branch uniting the melting-points of bismuth and antimony.
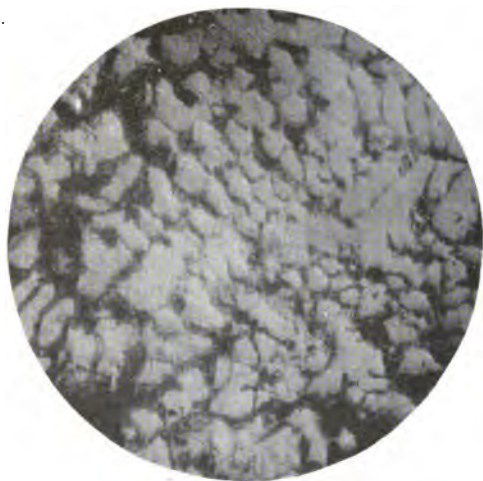
FIG. 12. Alloy of Antimony and Bismuth.
40 per cent bismuth. Magnified 60 diameters.

The hardness of these alloys also varies continuously with the composition; this continuity is also found in their microstructure. The forms of the crystals which compose these alloys vary slowly, assuming more and more the appearance of crystals of bismuth or of antimony, according as the former or the latter metal predominates. Their crystalline forms, however, are too ill-defined to be measured in any way.

The examinations of these alloys reveal a peculiarity which seems to be characteristic of isomorphous mixtures; the crystalline structure may be distinctly seen after polish-

ing, but while in the case of the alloys previously examined hard portions are seen, standing in relief and surrounded by a softer substance, which are dug out by the polishing operation, these alloys of bismuth and antimony exhibit rounded reliefs whose edges are not sharply outlined. Their appearance is suggestive of that of mountain-ranges in a relief-map. It would seem as if the hardness of the crystals and, therefore, their composition varies continuously, and the constitution of such alloys might be conceived as resulting from the following phenomena : When the solidification-point is reached, the edges of the crystals are formed by the solidification of the less fusible metal, antimony, the crystals then increase through the deposition of a mixture of the two metals whose percentage of bismuth gradually increases. Such deduction is confirmed by the appearance of the alloy after having been oxidized by heat, by etching with nitric acid, or by electrolysis. The softer portions, i.e., those that have been dug by the polishing, are then first colored and the coloration extends gradually over the whole surface, without, at any time, exhibiting any discontinuity in the course of the phenomenon. Fig. 12 shows the structure of an alloy containing 40 per cent of bismuth, magnified 60 diameters, and partially oxidized by electrolysis; the white crystals correspond to the hardest portions; they are gradually colored when the electrolysis is prolonged. When the preparation is heated intensely, the soft portions sink and unite to form small globules, while the hard edges of the crystals still remain solid ; they are, therefore, the most fusible and consequently the richer in bismuth.

[To be concluded in the next number of *The Metallographist.*]

MAGNETIC PROPERTIES OF HARDENED STEELS.*

By Mrs. SKLODOWSKA CURIE.

INTRODUCTION.

THIS investigation was undertaken with a view of ascertaining the influence of the chemical composition of steel upon its magnetic properties and the manner in which these properties are modified by the conditions of hardening. Those steels which are suitable for the manufacture of good permanent magnets have been studied more thoroughly. Finally the influence of a gentle tempering of the same steels, and the influence of vibrations and of time upon their magnetization have also been studied.

Prof. Le Chatelier placed at my disposal, for the above purpose, samples of various steels which had been analyzed. They were generally in the shape of bars 20 centimeters long, with a cross-section 1 centimeter square. In the case of certain steels, however, bars of other dimensions were used. A few steels were also examined in the shape of rings, forming closed magnetic circuits.

To characterize the magnetic properties of a certain steel, the bars were magnetized to saturation and the following factors determined:

1. The coercitive field.
2. The intensity of the residual magnetization in the middle of the bar.

Let ABCDB'C'A (Fig. 1) be the curve which represents the intensity of magnetization I in function of the magnetizing field H, for a closed magnetic circuit, such as a ring of steel. The field is produced by a current circulating in a wire wound regularly around the ring. As the field varies continuously from $+ H_1$ to $- H_1$, and from $- H_1$ to $+ H_1$, the intensity of

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magnetization assumes successively the values represented by the ordinates of the branches ABCD and DB'C'A of the curve. To the maximum value H_1 of the magnetic field H corresponds the maximum value I_m for the *intensity of the induced magnetization*, which is represented by the ordinate of the point A. When the field is null, the *intensity of residual magnetization* $I_r = OB$. The field being negative for a value $OC = H_c$, the ring will then be entirely demagnetized. H_c will be the *coercitive field* (this quantity is often called coercitive force). The knowledge of the whole curve is necessary to define the magnetic properties of a piece of steel. Yet the three factors: intensity of maximum induced magnetization I_m; intensity of residual magnetization I_r; and coercitive field H_c, suffice

Fig. 1.
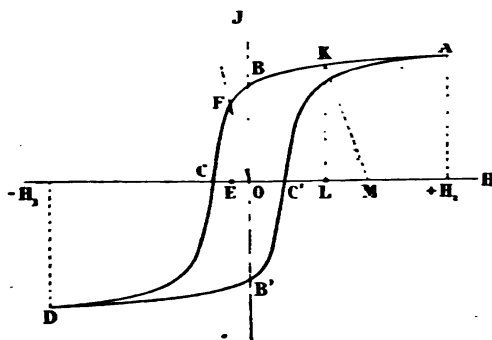
to characterize quite satisfactorily the nature of steel from this point of view.

In the case of a bar placed in a uniform magnetic field H′ and set in a direction parallel to that of the field, the magnetizing field H, at each point is the result of the superposition of the field H′ and of the demagnetizing field H″, due to the magnetization of the bar. If, after having magnetized the bar, the field H′ is suppressed, only the demagnetizing field H″ due to the poles remains. Let OE be the value of this field in the middle of the bar, EF will represent the *intensity of residual magnetization* I'_r *in the middle of the bar.*

The intensity of residual magnetization of a bar is always less than that of a ring, and is the nearer to it, the greater the

ratio between the length of the bar and its section. When that ratio is very great, the point F is very near B; when it is very small, F is near C, and the intensity of residual magnetization is nearly null. The external demagnetizing field for which the intensity of magnetization at the middle of the bar is zero, was determined and will be called the *coercitive field of the bar*. The coercitive field of a bar is nearly the same as that of a closed circuit. Indeed, at the moment the bar is demagnetized, the demagnetizing field is equal to the external field.

This proposition is not strictly correct, because all the portions of a bar are not demagnetized at the same time.

Our investigations have not revealed any systematic difference between the coercitive fields determined in the same steel in the shape of a bar and of a ring.

The coercitive field of a certain steel plays an important part when its adaptability to the construction of magnet is to be estimated. The intensity of residual magnetization in a closed circuit has, indeed, the same value in the case of a great number of steels, and even in the case of soft iron. The coercitive field, on the contrary, in the case of a very soft steel may be less than one, while it may be above 80 for certain hard steels. Those steels which have a weak coercitive field cannot, therefore, be utilized for the construction of permanent magnets. Their magnetization in an opened magnetic circuit is weak, since the demagnetizing field which results from it must be inferior to the coercitive field. The stability of magnets under the action of magnetic perturbations increases with the value of the coercitive field, as does also the stability of the residual magnetization under the influence of shocks and vibrations.

Measuring Methods.

BARS.

The following quantities may be measured:

1. The total magnetic moment of the bar M.

2. The flux of induction ϕ which traverses the cross-section of the middle of the bar.

3. The coercitive field.

As the bar is not uniformly magnetized, the intensity of the residual magnetization (residual magnetic moment per unit of volume) varies from one point to the next. The ratio of the total magnetic moment to the volume of the bar gives the mean value (I mean) of the axial component of the intensity of magnetization. · This quantity, so complex with regard to the properties of the substance, was determined only in the case of a few bars.

The flux of induction ϕ being known, the intensity of magnetization I in the middle of the bar may be calculated. This quantity was measured in the case of each bar; it bears
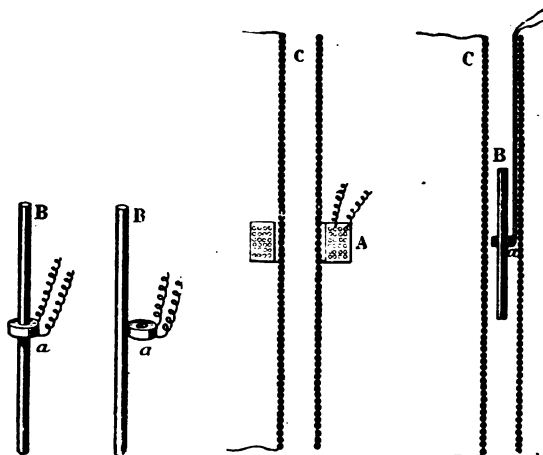
FIGS. 2 AND 3.   FIGS. 4 AND 5.

a simpler relation to the magnetic properties of steel; the determination of the flux, moreover, is more rapid than that of the magnetic moment.

When the bar is very long compared to its section, the values of I mean and of I in the middle of the bar are nearly equal. For the dimensions of the bars used, I mean is decidedly inferior to I in the middle of the bar. The coercitive field was determined in the case of all the bars.

The bars were all magnetized in a coil traversed by a current having a field of about 700 units, more than enough to produce saturation; a field of 1500 units did not produce a higher residual magnetization.

Determination of the Magnetic Moment. — The method employed was that of Gauss. The magnet under examination acted on a small magnet suspended by a cocoon-thread, and, in order to increase the sensibility, the terrestrial field was considerably diminished by means of a directive magnet. The magnetic moment of the bar was obtained by substituting for it a solenoid traversed by a known current and producing the same action as the magnet. The magnetic moment of the solenoid may be easily calculated.

Determination of the Intensity of Magnetization at the Middle of the Bars. — The absolute value of the flux of induction in the middle of each bar must be determined. This is accomplished by comparing the flux of the bar to a flux which may be calculated and which is furnished by a solenoid C (Fig. 4) traversed by a current and surrounded by the spirals of co-axial bobbin A. The determination is based upon the knowledge of the absolute values of the dimensions of the solenoid and of the intensity of the current. The latter, in turn, is the result of a resistance and an electro-motive force.

The measurement of the absolute value of the flux was made only in the case of a few bars which then were used as standards of flux, their constancy having been several times verified in the course of these experiments. The flux of the other bars was estimated by comparison with that of the standard bars.

The absolute value of the flux of a certain bar was determined as follows :

Two coils *a* and A are introduced into the circuit of a balistic galvanometer. The magnetized bar B being held vertically, the bobbin *a* is placed at its middle and then allowed to fall. The balistic deviation of the galvanometer indicates the values of the flux in the middle of the magnet.

The coil A (Fig. 4) is traversed by a co-axial solenoid C. This solenoid, which is very long, is formed by a single layer of wire carefully and uniformly wound. The bobbin is short and is covered by several layers of wire. When a current *i* circulates through the solenoid, the flux ϕ, which traverses the bobbin, may be calculated, introducing in the calculation the corrections due to the action of the ends of the solenoid C upon each of the layers of A.

At the instant when the current *i* is broken or closed, the variation of the flux ϕ produces an induction current in the circuit of the galva-

nometer. The intensity i of the current traversing the solenoid is regulated, so that when the current is broken, the balistic deviation is the same as that corresponding to the magnet. ϕ is then equal to the flux of the magnet.

i must be known in order to calculate ϕ.

To measure i, the difference in potential of this current for a known resistance is compared to that of a Latimer Clark cell and to that of a Gouy cell by the method of the potentiometer with resistance-box.

The bars whose flux was thus determined had been magnetized for several years. They were protected against vibrations and magnetic influences during the experiments. The magnet which was used in nearly all measurements is a cylindrical bar 23 centimeters long and 1 centimeter in diameter; for fifteen months the flux of that magnet did not vary $\frac{1}{300}$.

In order to measure the flux ϕ at the center of any bar, it was compared by the balistic method to the flux of one of the standard bars. The arrangement shown in Fig. 2 was used with the same coil placed in the circuit of the balistic galvanometer, the deviations produced by both bars being then compared.

Knowing ϕ, the value of the intensity of magnetization I at the center of the bar may be calculated. Let s be the section of the center of the bar, s' the mean surface of the spirals of the coil a, n the number of spirals, h the demagnetizing field at the center of the bar due to the pole; we have

$$\phi = 4 \pi n Is - nhs'.$$

The term nhs' for the bars employed is always very small relatively to $4 \pi n Is$, and constitutes a correction which is approximately determined as follows:

The bobbin a (Fig. 3) is placed by the side of the bar, near the center, and is allowed to fall. The resulting deviation is very nearly the measure of the flux nhs'; for h, in air, is at this place very nearly equal to h in the center of the bar. The correction for the bars used reached in some instances $\frac{1}{50}$ of the quantity to be measured. The value of I is then deducted from the formula.

Measurement of the Coercitive Field of the Bars. — The bar B (Fig. 5) is placed in the middle of a very long coil C and in the direction of its axis. A current circulates, in the proper direction, in the coils of the bobbin, producing a uniform field

which exerts a demagnetizing influence on the bar. The current is gradually increased from zero to the value for which the bar is demagnetized; the field existing then in the bobbin is the coercitive field.

In order to follow the state of magnetization of the bar, a small coil *a*, which is in the circuit of the balistic galvanometer, surrounds it in the middle. To ascertain the condition of the bar, the bobbin *a* is suddenly separated from it and pulled out of the bobbin C by means of a string. The bobbin *a* is guided by two copper-wires in such a way that upon releasing the string it will assume its former place (Fig. 5) without any disturbance of the apparatus being required.

When the bar is no longer magnetized, its presence does not modify the field produced by the current. It is, therefore, necessary to determine the current *i*, for which the flux in the bobbin is the same as when the bar is removed.

The deviation, when the magnet is removed, is proportional to the current. In a preliminary experiment, the value of that deviation per ampere is determined. It is relatively very faint, so that the value of the current which nullifies the magnetization differs little from that which nullifies the deviation.

When the bar is in the field, the balistic deviations indicated by the galvanometer, and corresponding to increasing values of the current, are recorded. The two neighboring values of *i*, which correspond to small deviations in opposite direction, as well as the deviations themselves are also noted. From these deviations are substracted algebraically those caused by the current of the bobbin alone. In this way, the deviations due to the magnetization are obtained, and the value of *i*, for which the magnetization is null, is calculated by interpolation. The corresponding field is the coercitive field of the bar.

The correction resulting from the field of the bobbin may be neglected in the case of bars with weak coercitive fields, but it must be taken into account in the case of magnet-steel.

Very small deviations only must be used for the calculation. The measurement is done tentatively. The current, however, cannot be diminished, because then the curve of cyclic magnetization would no longer be the same. If the current used was too strong, the bar must be remagnetized and the operation repeated.

The current *i* was measured by means of an accurate ampere-meter constructed by the firm of Chauvin & Arnoux. The instrument is always used in connection with shunts carefully standardized, by which means
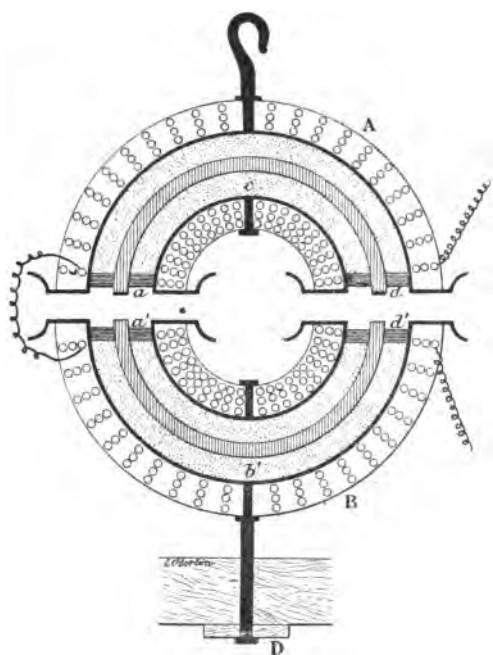
Fig. 6.
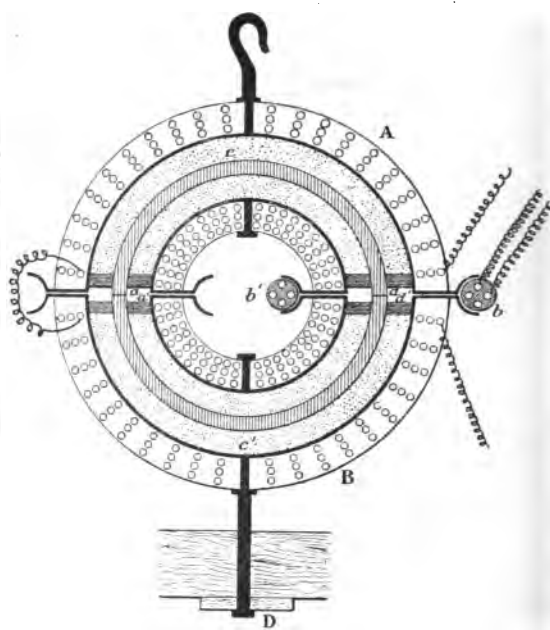
Fig. 7.
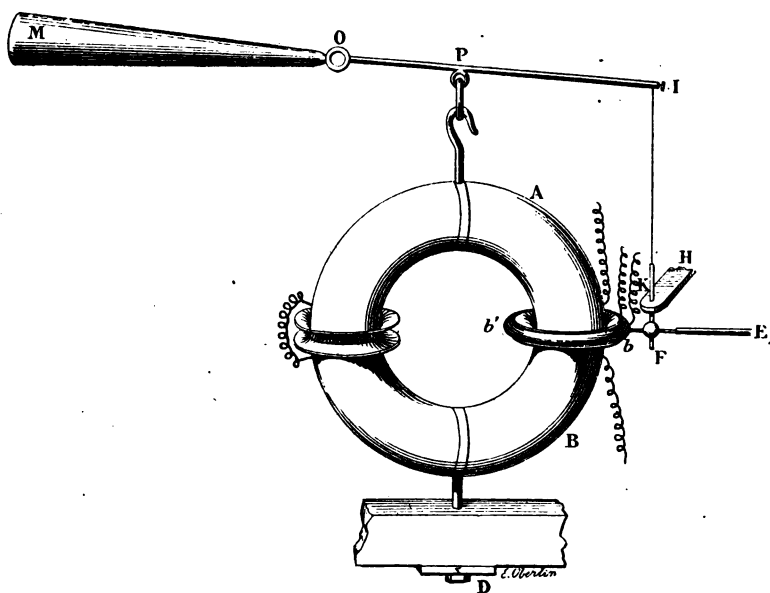
Fig. 8.

the degree of sensibility desired may be obtained. The very small corrections which must be introduced in the readings of this ampere-meter were determined several times during the course of the experiments. They were estimated from the knowledge of a resistance and of the electromotive force of Gouy and Latimer Clark standard cells.

RINGS.

Each ring was made up of two halves whose ends were carefully dressed and polished, so that both halves could be placed in very close contact. The rings had an average diameter of 11 centimeters and a cross-section of 1 square centimeter.

To produce a magnetic field in the rings, a coil was used composed of two semi-annular coils A and B (Figs. 6 and 7). The half-rings *acd*, *a'c'd'* were held in place inside the coils by means of sand represented by dotted areas in Figs. 6 and 7, corks being used at the extremities *a*, *d*, *a'*, *d'* of the rings to prevent the sand from running out. In Fig. 6 the half-rings are separated, in Fig. 7 they are united, so as to form a closed magnetic circuit. The mean field of the ring is $2\dfrac{Ni}{x}$, N being the total number of spirals, *i* the intensity of the current, and *x* the mean half-diameter of the ring.

The induced bobbin *bb'* (Figs. 7 and 8), which is in the circuit of the galvanometer, is introduced between the two halves of the annular bobbin. N is traversed by the magnetic flux ϕ due to the current circulating in the annular bobbin and to the magnetization of the ring. Its value is given by the equation:

$$\phi = 4\pi Is + \phi',$$

s being the section of the ring, I its intensity of magnetization, ϕ' the flux due to the field of the bobbin alone.

The flux ϕ, corresponding to a given current *i*, may be measured with the galvanometer by separating suddenly the two semi-annular coils and drawing out of the field, at the same time, the bobbin *bb'*. The circuit of the galvanometer includes also the small coil *a*, which takes up the flux of the standard magnet in order to determine the sensibility of the galvanometer.

The upper semi-annular bobbin A is suspended to a lever MP (Fig. 8) by means of a hook. The lower half of the bobbin is fastened permanently in D. The lever turns freely around the fulcrum O. When the handle M is lifted, the two halves of the bobbin are brought in perfect contact, while, when it is left to itself, the heavy handle falls by its own weight, lifting at the same time the upper half of the coil to a distance of a few centimeters above the lower half. The coil bb' is maintained in place by means of a rod KF, which is kept vertical by the board H through which it slides. When the upper half of the arrangement is lifted, the wire IK, fastened to the lever and to the rod FK, raises the bobbin bb' a small distance ; at the same time a stretched rubber-cord EF, to which the bobbin bb' is attached, pulls the latter out of the field. The complete operation takes place very rapidly and thus permits the use of the balistic method.

To calculate I, the flux ϕ' due to the bobbin alone must be known. It is proportional to the current, and its value per ampere is determined by repeating the above experiment after having removed the ring.

In order to construct the curve of magnetization, the current is made to vary progressively between $+ i$ and $- i$, in a cyclic manner. To obtain one point of the curve, the value of the flux corresponding to a certain value of i is measured ; the current is then allowed to travel over one cycle before determining another point.

HEATING, HARDENING, TEMPERATURE OF MAGNETIC TRANSFORMATION.

The bars were first heated by means of a gas-furnace, in a bath made up of a mixture of melted potassium-chloride and sodium-chloride.

An electric furnace was then used, similar to that employed by Mr. Charpy, but without rotating motion.*

The bar was placed in a porcelain-tube heated by means of a coil of platinum-wire traversed by a current. To avoid the cooling of the tube, it was introduced in a large clay-muffle, and the space between the two packed with calcined magnesia. This method of heating offered, in this case, a feature of special interest : the current caused the magnetization of the bar, and a small magnetic needle, mounted upon a pivot and placed near the furnace, opposite one of the poles,

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* *Bulletin de la Société d'Encouragement,* 1895, p. 670.

would assume, under the action of the bar, a direction at right angle to the terrestrial field to which the furnace was parallel. (The field of the current had nearly no action upon the needle.)

At high temperatures, steel is no longer ferro-magnetic, and the needle assumes again the direction of the magnetic meridian. As the transformation takes place, the needle is seen to change its direction, and the temperature at which such change occurs may be ascertained. *This temperature is precisely that which must be passed in order to harden a bar.*

The rings and some of the bars were also treated in baths of melted chlorides heated electrically by means of a coil of nickel-wire. The temperature of the bath may in this way be carefully regulated. It was found that nickel-wire could be used very satisfactorily for the construction of electric furnaces, instead of platinum-wire which is so much more expensive.

The temperature was ascertained by means of a Le Chatelier couple and a galvanometer. The following temperatures were selected for the graduation:

<div style="text-align:center">

Boiling-point of sulphur . . . . 445° C.
Melting-point of gold . . . . . 1050° C.

</div>

and it was assumed that between these two temperatures the curve resulting from temperatures and corresponding deviations was a straight line.

The melting-point of sodium-chloride is then found to be 772° C., and the temperature at which the magnetic transformation of iron occurs, 745° C.

The deviation of the galvanometer corresponding to the melting-point of gold is determined with great accuracy as follows: the welded end of the couple is wrapped in a very small piece of gold-leaf and placed in the middle of a small porcelain-tube electrically heated. The temperature of the couple may thus be brought gradually to a temperature giving a certain deviation without danger of exceeding it. The current is then shut off, and it is ascertained whether the gold has been melted; after a few similar trials the deviation corresponding to the fusion of gold is known accurately.

Experimental Results.

Steels Examined. — The steels examined contained various percentages of carbon and only a small amount of other impurities. They were obtained from the steelworks of Firminy, of Unieux, and of Boehler of Styria.

Special steels were also studied, containing different amounts of carbon and a certain percentage respectively of boron, copper, silicon, manganese, nickel, tungsten, and molybdenum from the Châtillon and Commentry, and Commentry and Fourchambault companies; some chromium-steels and tungsten-steels of the Assailly steelworks, and some tungsten-steels from the Allevard works and from the firm Boehler of Styria were also examined. The complete analyses of these steels are shown in Table I.

TEMPERATURE OF MAGNETIC TRANSFORMATION AND HARDENING TEMPERATURE.

Temperature of Magnetic Transformation. — It has been seen how the magnetization induced in a bar by the action of the heating current could be followed by means of a magnetic needle. When the bar is heated to a certain temperature, the induced magnetism falls rapidly to a very low value. It is called the temperature of *magnetic transformation.* When the bar is allowed to cool, an inverse transformation takes place, but generally at a temperature lower than the former; it is a case of hysteresis. We must, therefore, consider the temperature of the magnetic transformation during heating, and the temperature of the inverse transformation during cooling. It must be noted, however, that the magnetic transformation is not absolutely sudden, but seems to cover a certain number of degrees. This can be ascertained by maintaining the temperature stable in the middle of the transformation, in which case the transformation stops and the needle remains in a constant, half-deviated direction. That temperature, which in every case corresponded to a partial transformation producing the same deviation of the needle for the same current, was adopted as the temperature of transformation. In this way the observations recorded with bars of different nature were made comparable as much as possible.

TABLE I. — *Chemical Composition of the Steels.*

BRAND		SPECIAL ELEMENT	CAR-BON	SIL-ICON	MAN-GA-NESE
Carbon-steel, Firminy		—	0.057	0.053	0.13
			0.205	0.076	0.15
			0.493	0.045	0.24
			0.845	0.130	0.24
			0.837	0.135	0.24
			1.206	0.112	0.21
Carbon-steel, Unieux		—	0.747	0.057	0.15
			0.802	0.061	0.15
			0.829	0.091	0.19
			0.960	0.065	0.15
			1.405	0.075	0.14
			1.411	0.093	0.14
			1.609	0.076	0.13
Carbon-steel, Boehler of Styria	soft	—	0.699	0.316	0.47
	medium-hard	—	0.959	0.274	0.41
	extra tenacious hard	—	0.994	0.278	0.18
	extra medium-hard	—	1.166	0.443	0.32
		Tungsten			
Allevard steel	1st sample	5.52	0.591	0.018	0.32
	2d sample	4.92	0.617	0.027	0.27
Tungsten-steel, Assailly	V_4 .	2.917	0.551	0.201	0.42
	V_2 .	2.717	0.760	0.298	0.44
	V_3 .	2.696	1.107	0.322	0.38
Special steel, very hard, Boehler of Styria		2.870	1.101	0.163	0.27
		Chromium			
Chromium-steel, Assailly	C_1 .	2.486	0.501	0.273	0.23
	C_2 .	2.831	0.819	0.274	0.21
	C_3 .	3.445	1.069	0.363	0.21
		Nickel			
Nickel-steel, Fourchambault	Ni_4 .	3.616	0.567	0.176	0.34
	Ni_2 .	3.029	0.702	0.186	0.34
	Ni_3 .	3.732	1.214	0.280	0.32
Manganese-steel, Fourchambault	A .	—	0.464	0.161	0.69
	B .	—	1.183	0.882	1.83
	C .	—	1.941	0.984	2.20
Silicon-steel, Châtillon and Commentry	I. .	—	0.91	0.11	0.44
	II. .	—	0.91	0.64	0.54
	III. .	—	0.72	1.28	0.70
		Boron			
Boron-steel, Châtillon and Commentry	b .	0.5	1.05	0.16	0.29
	c .	0.8	0.97	0.09	0.26
Copper-steel, Châtillon and Commentry		Copper 3.95	0.87	0.03	0.28
		Tungsten			
Tungsten-steel, Châtillon and Commentry	a .	3.17	0.77	0.03	0.21
	b .	2.70	1.02	0.04	0.22
	c .	3.52	1.53	0.04	0.31
Allevard steel		5.84	0.59	0.09	0.58
Boreas-steel, Boehler of Styria		7.75	1.96	0.34	1.98
		Molybdenum			
Molybdenum-steel, Châtillon and Commentry	A .	3.48	0.51	0.08	0.34
	B .	3.36	1.25	0.03	0.21
		4.05	1.24	0.03	0.22
	C .	3.91	1.72	0.04	0.33

The rate of heating, or of cooling, does not seem to have any influence upon the temperature of transformation, provided the speed is not very great.

In the case of the Firminy carbon-steels, the temperatures given in Table II are the means of a great number of observations, made, for each grade of steel, on two or three different bars. In the case of the Unieux steels, one bar only of every grade was examined, and two or three observations only were made with each bar; errors of individual experiments have therefore more importance in the case of the latter series.

TABLE II. — *Temperature of the Magnetic Transformation of the Steels.*

KIND	BRAND			% C.	t	t'	$t-t'$
Carbon-steels	Firminy			0.06	745	741	4
				0.20	739	734	4
				0.49	733	721	17
				0:84	729	681	50
				1.20	725	698	27
	Unieux			0.75	732	692	40
				0.80	726	698	28
				0.83	723	700	23
				0.96	728	696	32
				1.40	722	693	29
				1.41	721	699	22
				1.61	717	690	27
				% W.			
Tungsten-steels	Assailly	V_1	2.9	0.55	750	708	42
		V_2	2.7	0.76	746	714	32
		V_3	2.7	1.11	725	687	38
	Châtillon and Commentry	c	3.5	1.53	722	696	26
		b	2.7	1.02	721	684	37
	Allevard	—	5.5	0.59	740	705	35
	Boehler	—	7.7	1.96	732	697	35
			% Mo.				
Molybdenum-steels	Châtillon and Commentry	A	3.5	0.51	730	686	44
		B	3.4	1.25	730	689	41
		C	3.9	1.72	710	683	27
			% B.				
Boron-steels	Châtillon and Commentry	b	0.5	1.05	727	695	32
		c	0.8	0.97	728	684	44
			% Cu.				
Copper-steel	Châtillon and Commentry	—	3.9	0.87	701	658	43
			% Cr.				
Chromium-steel	Assailly	c_3	3.4	1.07	746	727	19

t = temperature of magnetic transformation during heating.
t' = temperature of magnetic transformation during cooling.

The experiments are not sufficiently accurate to lead to very complete conclusions. The temperatures stated in degrees have been tabulated, because they are in certain cases the averages of several experiments, but the uncertainty of individual determinations may amount to more than 10 degrees. We may, however, notice: (1) that the temperature of transformation during heating falls with the percentage of carbon; (2) that the difference between the temperatures of transformation during heating and during cooling is very small (only a few degrees) in the case of slightly carburetted steels, increasing at first with the amount of carbon, and apparently reaching a maximum (40 to 50°) for a carbon-content of about 0.8 per cent.

Necessary Condition for the Hardening of Steel. — In order to be hardened (*prendre la trempe*), steel must be quenched at a high temperature while it is in a feebly magnetic condition. It is found that if a steel-bar be heated to a temperature lower than that of the magnetic transformation which takes place during heating, it does not harden through sudden cooling (quenching in cold water). On the contrary, if the bar be heated to a temperature higher than that of the magnetic transformation, it does harden through sudden cooling. After the transformation which occurs during heating has taken place, the bar may be allowed to cool a certain number of degrees before quenching, and it will still harden as long as it has not been cooled to a temperature lower than that of the magnetic transformation occurring during cooling. As an instance of this phenomenon, the variations of the magnetic properties of a steel-bar containing 0.84 per cent of carbon and quenched under different conditions are shown below. H_c indicates the coercitive fields, I_r the intensities of residual magnetization. The bar was 20 centimeters long and had a cross-section 1 centimeter square.

Temperature of magnetic transformation during heating, 730° C.
Temperature of magnetic transformation during cooling, 680° C.

	H_c	I_r
Steel annealed	8	85
Steel quenched at 705°, when magnetic	14	130
Steel quenched at 770°, when non-magnetic	52	410
Steel quenched at 690°, when non-magnetic (after heating to 800° followed by slow cooling)	50	380

TABLE III. — *Influence of the Quenching Temperature. Carbon-steels.*

				T	Hc	Ir
FIRMINY STEELS. — *Bars 20 cm. in length and 1 cm. square.*						
C = 0.06 %	Bar 1.	1st quenching	. . . . .	795	2.2	22
		2d -	. . . . .	915	3.0	24
		3d -	. . . . .	1025	3.4	31
C = 0.20	Bar 1.	1st quenching	. . . . .	785	8	96
		2d -	. . . . .	825	11	113
		3d -	. . . . .	885	11	114
	Bar 2.	1st quenching	. . . . .	840	11	118
		2d -	. . . . .	915	10	108
		3d -	. . . . .	840	10	107
		4th -	after cycle .	840	11	112
C = 0.49	Bar 1.	1st quenching	. . . . .	770	23	222
		2d -	. . . . .	835	23	213
	Bar 2.	1st quenching	. . . . .	835	20	195
		2d -	. . . . .	920	16	160
		3d -	. . . . .	780	20	208
C = 0.84	Bar 1.	1st quenching	. . . . .	750	54	416
		2d -	. . . . .	830	48	378
		3d -	. . . . .	765	52	426
	Bar 2.	1st quenching	. . . . .	830	49	379
		2d -	. . . . .	770	53	426
		3d -	. . . . .	975	48	358
		4th -	. . . . .	770	50	376
		5th -	after 2 cycles	770	52	387
	Bar 3.	1st quenching	. . . . .	760	52	412
		2d -	. . . . .	800	48	386
		3d -	. . . . .	730	53	411
		4th -	after 3 cycles	765	53	400
C = 1.20	Bar 1.	1st quenching	. . . . .	760	57	430
		2d -	. . . . .	745	54	400
		3d -	. . . . .	725	54	399
		4th -	. . . . .	770	51	384
		5th -	cycle . . .	770	60	451
		6th -	. . . . .	905	48	264
	Bar 3.	1st quenching	. . . . .	770	39	335
		2d -	. . . . .	770	41	337
		3d -	cycle . . .	770	59	454
		4th -	2 cycles . .	770	60	468
		5th -	. . . . .	770	55	397
		6th -	2 cycles . .	770	58	441
UNIEUX STEELS. — *Bars 20 cm. in length and 1 cm. square.*						
C = 0.75		1st quenching	. . . . .	770	51	414
		2d -	. . . . .	795	51	393
C = 0.80		1st quenching	. . . . .	755	53	421
		2d -	. . . . .	810	51	370
		3d -	. . . . .	810	49	366
C = 0.83		1st quenching	. . . . .	770	56	440
		2d -	. . . . .	810	52	375
C = 0.96		1st quenching	. . . . .	775	58	431
		2d -	. . . . .	805	54	381
Bars 20 cm. in length and 0.85 cm. square.						
C = 1.40		1st quenching	. . . . .	800	62	479
		2d -	. . . . .	750	57	468
		3d -	cycle . . .	750	61	505
C = 1.41		1st quenching	. . . . .	800	62	462
		2d -	. . . . .	745	47	404
		3d -	cycle . . .	745	60	494
C = 1.61		1st quenching	. . . . .	800	31	278
		2d -	cycle . . .	750	46	375

T = quenching temperature. — Hc = coercitive field. — Ir = intensity of
the residual magnification of the bar.

The 1st quenching had little effect; the steel was, at the time of sudden cooling, in the ferro-magnetic condition, since the temperature had not reached 730°. The 2d and 3d quenchings acted energetically; the bar was only feebly magnetic, as its temperature had been raised above 730° and had not been allowed to fall again below 680°. In this way the 3d quenching was much more effective than the 1st, although taking place at a lower temperature.

Influence of the Quenching Temperature upon the Magnetic Properties of Carbon-steels. — This influence has been studied in the case of carbon-steels, and its results are tabulated in Table III. The following conclusions may be drawn:

In the case of very soft steel containing 0.06 per cent of carbon, the coercitive field and the residual intensity increase with the quenching temperature, as the latter varies from 800° to 1025° C.; it is beneficial, therefore, to quench at a high temperature.

In the case of soft steels containing 0.20 per cent of carbon, the quenching temperature has little influence between 785° and 915°.

With 0.5 per cent of carbon, the bars quenched between 770° and 835° have the same properties, but after quenching at 920° both the intensity of magnetization and the coercitive field are found to have decreased; it is therefore beneficial to quench below 830°.

With hard steels containing 0.84 and 1.20 per cent of carbon, the coercitive field and the intensity of magnetization decrease with the quenching temperature; it is therefore beneficial to quench at a low temperature, taking care, however, that the temperature of the magnetic transformation has been exceeded. Good results are obtained by heating the bars to 770°. In the case of the steel containing 0.84 per cent of carbon, heating it to a temperature of 975° modifies the metal permanently (burnt steel); for upon quenching it at 770° it is found that it has lost much of its magnetic properties. In the case of still more carburetted steels, a long heating at 800° produces a similar effect; the heating of high-carbon steels before quenching should therefore be of short duration.

Influence of the Cycles of Thermal Variations Taking Place before Quenching. — The cyclic variations of temperature

referred to here are made to take place between a temperature
a little lower than that of the magnetic transformation during
cooling and a temperature a little above that of the magnetic
transformation occurring during heating, in such a way that
the steel is made to undergo the two inverse transformations.
If a piece of steel be quenched in its non-magnetic condition,
after a cycle of this kind, the effect of the quenching is gen-
erally improved if the steel be highly carburetted.   This is
clearly shown in the case of the sample of Firminy steel con-
taining 1.20 per cent of carbon, and in all steels more highly
carburetted (Table III).   The effect of these cycles upon
high-carbon steels seems to be precisely the reverse of the
effect of a prolonged heating ; it seems to destroy partly the
alteration produced by a long heating.   Steels containing
less than 1 per cent of carbon are not generally affected by
these temperature-cycles.   In the case of the sample with 0.84
per cent of carbon, however, after it has been modified by too
high a temperature, the cycle seems to restore to it part of its
magnetic qualities.

COLD WORK AND QUENCHING.

It is known that, with regard to the tenacity, cold work
(*écrouissage*) has upon steel-wires an effect similar to that of
quenching.   It has been ascertained, on the contrary, that
with regard to the magnetic properties cold work acts much
less energetically than quenching.   The increase of the
coercive field produced by cold work is very small compared
to that due to sudden cooling.   Bundles of wires were used
for these experiments, containing each 5 or 6 wires 2 milli-
meters in diameter and 20 centimeters long, and made from
Firminy steel with 0.84 per cent of carbon.   Certain wires
were annealed, showing a tenacity of 60 kilogrammes per
square millimeter, others were quenched and others cold
drawn, the latter revealing then a tensile strength of 220 kilo-
grammes per square millimeter.   Their magnetic properties
are tabulated below :

	H_c	I_r	I_r
6 wires annealed	11	415	
6 wires cold drawn	16	780	
5 wires cold drawn	16		680
5 wires quenched	52		630

THIS important memoir of Mrs. Sklodowska Curie constitutes a most valuable addition to our knowledge of the magnetic properties of steel at various temperatures, and of the influence of various amounts of carbon and of certain special elements upon these properties.

The editor will venture to summarize briefly this first installment of the results of her investigations, and to offer a few criticisms.

In Vol. I. No. 1 of *The Metallographist*, page 27 and seq., the critical changes or transformations which occur in the
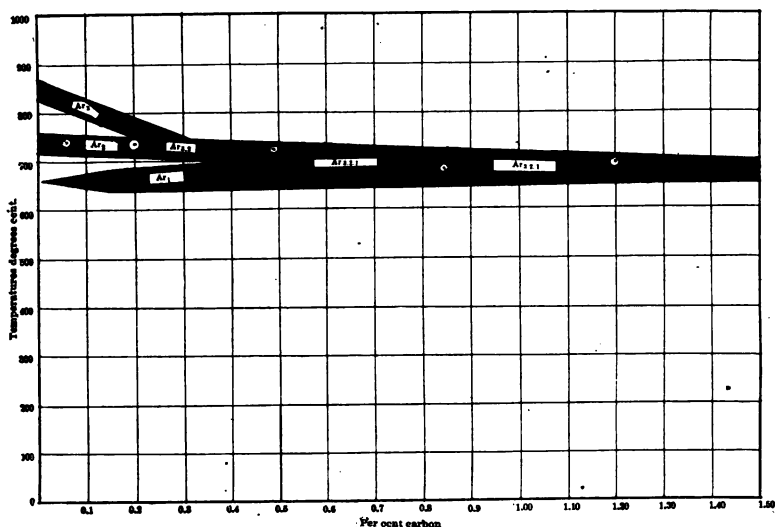
FIG. *a.*

constitution of steel during heating or cooling have been described. These transformations are accompanied by an absorption or an evolution of heat (the former during heating, the latter during cooling), which produces a "retardation" in the rate of heating or of cooling (the evolution of heat may be so considerable as to cause an actual rise in the sensible temperature of the cooling metal, a "recalescence"). The curve representing the rate of cooling or of heating of the steel exhibits distinct critical points corresponding to those transformations.

It has been seen that steels containing less than, say, 0.25 per cent of carbon have three distinct critical points A_3, A_2, A_1. With a carbon-content varying between, say, 0.25 and 0.45 per cent of carbon they have two retardations $A_{3\,2}$, A_1 (the two upper retardations occurring at the same temperature). Above 0.45 per cent of carbon they exhibit only one such critical point, $A_{3\,2\,1}$ (the three transformations occurring at the same temperature). This is well illustrated in Fig. *a*, which also indicates the temperatures during which the transformations take place (during cooling) and the ranges which they cover.

It had long been known that, at a high temperature, iron and steel lost their magnetic properties. Mrs. Sklodowska Curie has determined by numerous skillfully conducted experiments the temperature at which such momentous changes take place. The results obtained with carbon-steels have been plotted in Fig. *a*, where they are indicated by white circles. From their positions we naturally conclude that *the transformation which produces the second evolution of heat during the cooling of soft steel is also that which restores to it its magnetic properties*, thus identifying the critical point A_2 with the changes of magnetic properties. This conclusion which had already been reached is then fully confirmed by this recent inquiry.

On page 117, the authoress says, speaking of the temperature of magnetic transformation: "This temperature is precisely that which must be passed in order to harden a bar"; and on page 121: "In order to be hardened, steel must be quenched at a high temperature while it is in a feebly magnetic condition."

It would seem at first sight that the steel must indeed be in its non-magnetic condition in order to be hardened through sudden cooling, but is it, in reality, a necessary condition?

Let us take a piece of steel containing 0.30 per cent of carbon, and let us heat it to a high temperature and then cool it past the point A_2, quenching it, however, before the point A_1 has been reached, i.e., between A_2 and A_1. It will be hardened most decidedly,* although it was magnetic at the

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* While some additional hardening power is gained during the upper retardations A_3 and A_2, as was conclusively shown by Mr. Howe and others, a very great portion of the hardening power is acquired during A_1

time of quenching, since the transformation A_2, which restores the magnetic properties, had taken place.

In the case of steel containing less than some 0.45 per cent of carbon, there exists, it would seem, a narrow range of temperature, in which the steel, although being magnetic, possesses also considerable hardening power. This range of temperature, being comparatively very narrow, may easily escape detection.

The statement of the authoress infers that steel gains its hardening power during the retardation A_2, i.e., during the magnetic transformation, while numerous previous investigations have established quite conclusively that it is during A_1 (or $A_{3\,2}$, as the case may be) that it acquires most, if not all, of that power.

With over 0.45 per cent of carbon in the steel, and, therefore, for all grades of steel used in the construction of permanent magnets and for nearly all steels whose hardening power is utilized, the retardations A_1 and A_2, i.e., the magnetic transformation and that transformation which confers most of the hardening power, *occur at the same temperature*, but it does not follow that both transformations cannot take place independently. Indeed, from the evidences offered by the behavior of softer steels we are naturally led to infer that they are independent of each other, that *the steel must not necessarily be in a non-magnetic condition in order to be hardened by sudden cooling ;* that if, in the great majority of cases, it is in a non-magnetic condition when endowed with hardening power, it is a mere coincidence due to the fact that, in such cases, both transformations take place at the same temperature.

This question, however, is well worth further inquiry, and the editor hopes that his remarks will call forth the comments of those who have investigated it.

With regard to the temperature at which occurs the magnetic transformation in carbon-steels, the results of her investigations lead, as she remarks, to the following deductions :

1. The rate of heating or of cooling does not seem to have any influence upon the temperature of transformation, provided the speed is not very great.

2. The temperature of transformation during heating falls with the percentage of carbon.

3. The difference between the temperatures of transformation during heating and during cooling is very small in the case of slightly carburetted steel, and increases at first with the amount of carbon, apparently reaching a maximum (40 to 50°) for a carbon-content of about 0.80 per cent.

The last two propositions are well illustrated in Fig. *b*, in which have been plotted the results obtained by the authoress in the case of the Firminy carbon-steels, the figures tabulated representing the means of a great number of determinations.

Per cent carbon.

X = temperature of magnetic transformation during heating.
o = temperature of magnetic transformation during cooling.
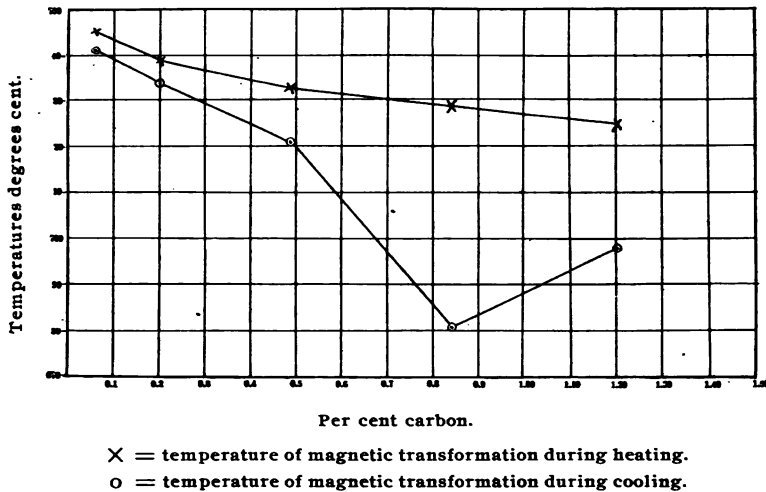
FIG. *b*.

It is interesting to recall that the difference between the position of the points A_1 and A_3 during heating and their position during cooling is greater than is the case for the transformation A_2. The former points are probably more affected, also, by the rate of cooling or of heating.

From her investigations concerning the influence of the quenching temperature on the magnetic properties of carbon-steels, the following conclusions are drawn:

In the case of very soft steel it is beneficial to quench at a high temperature.

In the case of soft steel (containing about 0.20 per cent of carbon) the quenching temperature has little influence.

With 0.50 per cent of carbon it is desirable to quench below 830° C.

High-carbon steel should be quenched at a low temperature, slightly above the temperature of magnetic transformation [which corresponds to its single retardation. — ED.]. The heating previous to quenching should be of short duration; a prolonged heating, even at a relatively low temperature, depriving the metal of much of its magnetic properties, which cannot be restored to any great extent.

The authoress also finds that the magnetic properties of high-carbon steel are improved to a marked degree by heating the metal to a temperature a little above that of the magnetic transformation, cooling it past the temperature of the inverse transformation, and finally reheating it to the desired quenching temperature. The effect of these cycles upon highly carburetted metals seems to be the reverse of the effect of a prolonged heating; it appears to efface, at least in part, the alteration produced by a long heating. Steel containing less than 1 per cent of carbon is not generally affected by these temperature-cycles.

It is also shown that, while the effect of cold work upon the tenacity of steel may in some cases be compared to that of quenching, with regard to the magnetic properties cold work acts much less energetically than sudden cooling. Cold working produces only a very small increase of the coercitive field, compared to that resulting from sudden cooling, the figures being: annealed 11, cold drawn 16, quenched 52.

This memoir will be continued in the next number of *The Metallographist*, and concluded in the October number.

The next installment will be devoted to the influence of the chemical composition upon the magnetic properties, the last to the permanency of magnetization in steel-bars, as affected by time, by shocks and vibrations, by variation of surrounding temperature and by the action of magnetic fields existing in the vicinity of the bar.   A. S.

STEEL AND IRON ALLOYS.*

By R. A. HADFIELD.

IN the use of iron the latest and not the least important phase of development is found in its alloys or compounds with other elements. This study is, perhaps, one of the most fascinating of all its branches of research and manufacture, and metallurgists devoted to this special branch are continually endeavoring to improve and strengthen their beloved " Ferrum " by giving it higher tenacity and elasticity, more ductility and greater hardness, without sacrificing the metal's valuable and inherent toughness.

There is no doubt that the metal iron in itself would be of little service to the world at the present day in face of requirements which necessitate a material possessing resistance to so much greater stresses and strains than formerly. Professor T. Turner has shown that the pure metal iron is not considerably harder than copper, and is not very much stronger as regards tensile strength; and it can be readily imagined how in itself such a metal would render impossible that combination of high speed with greater wear and tear for uses which are the result of modern mechanical developments of all classes. Without doubt, further developments in modern mechanical progress will largely depend upon the material which the experimentalists in question can offer for utilization by the mining, mechanical, or electrical engineer.

It need also hardly be said that such progress renders necessary a development which becomes each year more complex, and requires more specialization of research. The writer has therefore ventured in another paper presented to this conference to suggest a number of lines for research and investigation which it is hoped may be of service. The problems to be solved present a field in which results at all

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* Paper read at the Institution of Civil Engineers, Engineering Conference. Section IV. — Mining and Metallurgy.

approaching to finality are very far away, and can only be attacked little by little.

In a paper read by Professor Arnold before the Iron and Steel Institute, upon "The Physical Influence of Elements on Iron," he pointed out a number of interesting and valuable facts relating to alloy-steels. A series of 13 alloys were pre-

	C.	NI.	MN.	CU.	CR.	W.	AL.	SI.	AS.	P.	S.	FE.CAST
SPECIAL ELEMENT	99·87	1·35	1·51	1·29	1·81	1·10	1·41	1·85	1·84	1·57	1·36	·97	99·82
CARBON	·04	1·35	·11	·10	·10	·17	·08	·03	08	·04	·07	·08	08
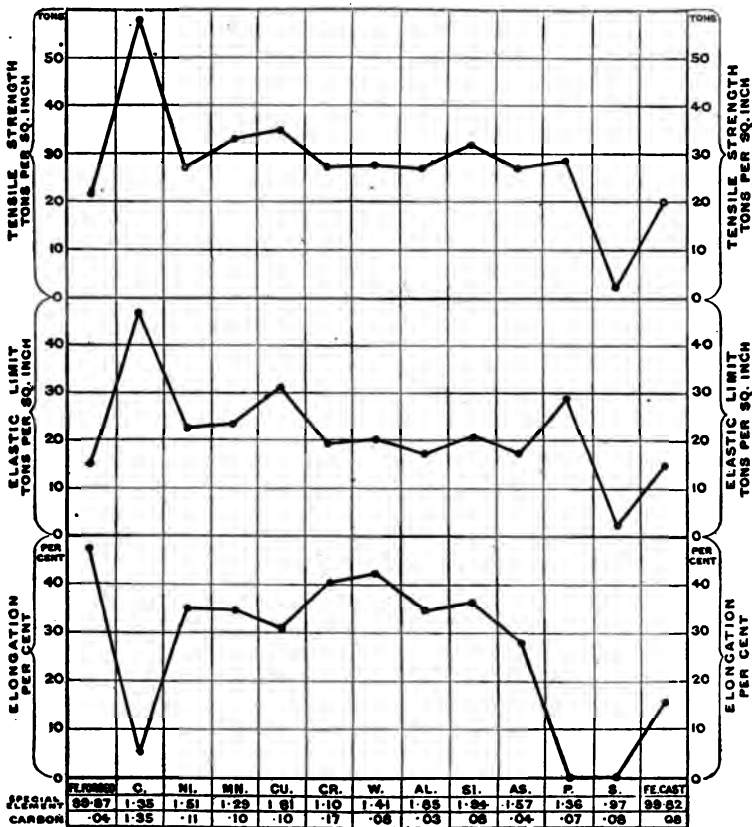
pared, including cast and forged pure iron, also iron alloyed respectively with as nearly as possible 1½ per cent of each of the following elements: carbon, silicon, aluminium, manganese, nickel, copper, chromium, tungsten, arsenic, phosphorus, and sulphur. A most exhaustive series of mechanical and microscopical tests were undertaken, offering a remark-

ably unique correlation. The writer has plotted Professor Arnold's data in the annexed diagram, as his results have not before been presented in this particular form. From this can be readily seen the particular effect of each element. Whilst these tests do not give the effect of wide variations in the percentages of each element upon iron, they are in themselves of the utmost service by showing the results obtained by the addition of one particular percentage, and that percentage not usually likely to be exceeded in practical use.

The properties of the principal iron alloy, carbon-steel, are well known, and only need a general reference here. Purity of material still holds the field for the production of the highest and best quality of carbon-steel. One of our honorary members, Sir F. Abel, by a number of valuable researches, contributed to the Iron and Steel Institute, the Mechanical Engineers, and other societies, has done specially important work in this direction. It is, therefore, a special satisfaction to know that the Iron and Steel Institute has wisely awarded him the prized recognition of the Bessemer Gold Medal. This work has also been continued and amplified by Professor Arnold, Messrs. Stead, Howe, Sauveur, Benneville, Hogg, and Spencer, and on the Continent by those exceedingly able investigators, Professor Ledebur and Dr. Müller.

One of the iron alloys which has been discussed so much during the last three or four years is nickel-steel. Whilst without doubt this material has certain special applications of great advantage, it will be probably found that it has itself no particular field. The writer has seen Harveyed armor-plates tested in which there was no nickel, which have given exceedingly good results, and probably equal to those containing nickel.

Nickel in the presence of carbon does no doubt considerably raise the elastic limit of iron, but its combination with carbon more than its direct influence upon the iron present has been much overlooked, or, perhaps, it would be more correct to say that the carbide of iron is rendered much more powerful by the presence of nickel. In other words, its action is not at all dissimilar to that of chromium.

The writer has prepared a novel alloy — cobalt-steel —

which has a number of interesting properties somewhat resembling those of nickel-steel. One specimen, containing 1.80 per cent cobalt, in its unannealed condition had a tensile strength of 41 tons, with an elongation of 19 per cent. After annealing, the tensile strength was reduced to 35 tons, with an increase of elongation to 29 per cent. With much higher percentages the alloy is still very malleable, and there is a distinct tendency to show higher elastic limits than ordinary carbon-steel, in this respect being somewhat similar to nickel-steel.

One of the special developments of alloy-steel has been the result of the writer's experiments in the production of manganese-steel, the first description of which he had the honor of laying before this Institution in 1888. There was no one who took more pains than the author to point out that manganese-steel, owing to its peculiarities, would require long and careful study to master the difficulties in its production and application. Happily these are gradually being overcome, and it presents an increasing application for a large number of purposes each year both in this country, the colonies, and America.

But alloys of manganese-steel present most perplexing anomalies, for while those containing from 3 per cent to 6 per cent in the presence of not more than 0.6 per cent of carbon give an exceedingly brittle and hard product, yet upon doubling the proportion of manganese, that is, to 12 per cent or 14 per cent, alloys possessing entirely different properties are obtained. Castings of this latter material, when suitably treated, possess a most extraordinary combination of hardness and toughness, which enables them to offer a higher resistance to abrasion than any alloy yet produced. The same material in the forged condition, also after suitable treatment, possesses tenacities of 60 tons to 70 tons per square inch, with high elongations, 35 per cent to 40 per cent. Yet these materials, whether in the cast or forged conditions, cannot be machined except with the greatest difficulty; in fact, their hardness approaches that of chilled iron. Here, again, these properties cannot be judged from the same standpoint as that of other metals possessing hardness, for such manganese-steel, while so hard to the machine-tool, can be indented with an ordinary hand-hammer; in other words, it

is not "glass-hard," but combines in a specially peculiar manner hardness and toughness.

It is very unfortunate there is such laxity of expression as regards this particular quality, "hardness." Such terms as "intensely hard," "extremely hard," and the like, unless used in the most guarded and careful manner, are often misnomers. During the discussion on Mr. A. Sauveur's valuable paper to the American Institute of Mining Engineers, Mr. R. G. Scott, of the Monkbridge Iron Works, Leeds, pointed this out. As he says, "Hardness is often given without the least definite idea as to where the specimen might be placed in the ordinary mineralogical scale of hardness; is it as hard as corundum, or does it approach the hardness of the diamond?" It would be of the highest importance to metallurgy if some definite method could be introduced.

Messrs. Jannettaz and Goldberg, of Paris, read their important paper before the French Institute of Civil Engineers in July last, "Mesures de la résistance à l'usure de quelques alliages de cuivre." The apparatus, termed a usometer, consists of a rotating disc upon which are mounted the specimens to be compared. More or less surface pressure can be produced by a method of attaching weights. The wear of the specimens is readily and accurately detected by accurate weighing before and after the test. From these results some very valuable data have been obtained, especially regarding those metals of softer nature and their alloys.

The system has also been extended to testing the hardness of various kinds of glass and enamels.

These gentlemen were good enough to test for the writer several specimens of carbon-steel, manganese-steel, and other alloy-steels, but the results, whilst of considerable interest, do not seem to show sufficient uniformity to draw exact conclusions. It is to be hoped, however, that their experiments will be continued, as an exact determination of hardness in an easy and simple manner is of the utmost importance to the practical metallurgist.

It is therefore of the utmost importance that metallurgists and engineers should come to some clear and definite understanding as to the meaning of the term "hardness"; an established definition of this property, so that comparisons

MICROSCOPIC STUDY OF METALLIC ALLOYS.*

By G. CHARPY.

THE microscopic study of metals has until now been
applied more especially to industrial alloys. These
researches have led to important results in the department of
technical metallurgy, but they imply few general deductions
concerning the constitution of alloys. This is due to the fact
that the metals which are of·industrial use are those whose
structures are most complicated. Alloys which are composed
of two metals simply in close contact possess naturally
properties which differ little from those of the metals, and so
they were empirically left aside in order to utilize the alloys
whose complex constitution renders it possible to obtain
properties superior to those of the component metals.

On account of this complexity, industrial alloys are not
well suited to furnish indications regarding the constitution of
metallic alloys; with that end in view, it is preferable to start
from alloys having a constitution as simple as possible, and
to approach gradually the most complicated cases. The
researches described in this memoir have been conducted
accordingly; we have taken as guide previous studies deal-

* Bulletin Société d'Encouragement pour l'Industrie Nationale,
March, 1897.

ing with the physical properties of alloys, and especially those dealing with the *curves of fusibility*, and which have been summarized by Mr. H. Le Chatelier in a series of articles * and by Mr. H. Gautier.†

I. Technology.

The samples to be examined through the microscope are first filed or ground on an emery-wheel, then rubbed on emery-papers of increasing fineness, and finally polished upon a very fine piece of chamois leather, using first some "brillant belge" and then a very small quantity of very fine jewelers' rouge.

The polishing of hard metals presents no great difficulties, but such is not the case for soft alloys, especially if they contain a large proportion of lead or tin; it is then impossible to obtain a specular polish, the soft metal spreading, very much like a fat substance, over the whole surface of the preparation. With care and patience, however, it is possible to produce surfaces upon which a proper chemical action outlines the structure with distinctness.

Polishing alone sometimes suffices to render visible the hardest constituents or those which are colored, but a chemical attack is generally required. While it is indispensable, when studying a certain alloy for the purpose of ascertaining the transformations produced by a certain mechanical or thermal treatment, to employ a well-defined and always identical etching-method, such is not the case when it is desired to characterize the various constituents of alloys; on the contrary, it is useful then to use successively different re-agents, the comparison of the results obtained in this way being one of the best means of ascertaining the nature of a certain constituent.

The re-agents most frequently used are the various acids, caustic potash, ammonia, and alkaline sulphides; they are used in the shape of very diluted alcoholic solutions, in order to destroy the action of fatty substances which sometimes remain on the surface of the preparation. The specimens are

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* *Bulletin Société d'Encouragement*, February, April, and May, 1895.
† *Idem*, October, 1896.

placed upon a platinum plate, thus giving rise to the formation of an electric couple, which greatly regularize the chemical action.

It is often possible to render the structure apparent by heating the metal in contact with the atmosphere; the various constituents are then oxidized successively and assume different colorations. As gaseous re-agent, hydrosulphuric acid should be noted; it gives good results with certain silver alloys.

Finally, the method most generally used consists in etching the preparation by electrolysis, by placing it in a saline solution and connecting it with the positive pole of a battery whose negative pole is connected with a platinum plate or wire.

[Mr. Charpy states here that the preparation must generally be examined by direct reflected light, i.e., by light reflected downwards along the axis of the microscope, and explains some of the appliances employed for obtaining such an illumination. They will be described exhaustively in an early number of *The Metallographist*. As a source of light, the writer used an incandescent lamp, and his objectives were Nachet's instruments. He also recommends the use of projection eye-pieces for photographic work. — ED.]

Microscopic examinations do not always permit to ascertain conclusively the nature of the various constituents which are revealed, but they furnish indications which, considered jointly with the properties of the same substances, would lead almost to a certainty.

The various constituents hardly ever occurring as wellformed crystals, but as *crystallites* with curved and ill-defined edges, the shape of the constituents can only give, in general, roughly qualitative indications.

The relative hardness of the various constituents furnishes one of the best means of distinguishing them; polishing upon a somewhat thick piece of chamois leather suffices generally to cause the hardest components to stand in relief; hard crystals are found even in alloys composed of soft metals; they are then unquestionably made up of a definite compound; such is the case for alloys of copper and tin, of silver and tin, etc.

Mr. Behrens has, in some instances, measured the relative hardness of two adjacent constituents by scratching them with needles made up of metals of known hardness.

The color of the constituents often furnishes useful information: a violet compound is found in alloys of antimony and copper; in alloys made up of copper and zinc, or of copper and tin, those parts which contain much copper are yellow, while those containing much zinc or tin are white, etc.

The method most generally applicable consists in study-ing the action of different re-agents upon the various microscopic constituents. In the case of lead and tin alloys, for instance, hydrochloric acid covers the crystals of lead with a white layer of chloride of lead, while it dissolves the tin; nitric acid, on the other hand, dissolves the lead and covers the tin with a white layer of metastannic acid. In the case of silver alloys, hydrosulphuric acid imparts a black coloration to those parts which contain most silver; when copper alloys are treated with ammonia, the areas rich in copper are oxidized first.

Finally, attention should be called to a somewhat unexpected method of investigation, which has been indicated for the first time by Mr. Albert Sauveur and applied to steel, i.e., the use of the planimeter.* It furnishes a means of measuring the areas occupied by the various constituents, thus giving, so to speak, a proximate analysis whose results, compared with those of ultimate analysis, afford valuable information. We have applied this method in several instances, and in the case of alloys of antimony and silver it has revealed the probable existence of a definite compound, because of the considerable gap existing between the calculated proportions of the various constituents and those actually observed.

Planimetric measurements are evidently only approximate; they suppose the alloy to be quite homogeneous, and, on that account, can better be applied to industrial metals than to alloys prepared in small quantities, for experimental purposes, and cast under conditions which generally allow segregation to take place; these measurements, however, are

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* See *The Metallographist*, Vol. I. No. 1 (January, 1898), page 39 and seq., for a short description of the use of the planimeter in micrographic work. — ED.

none the less very important; besides the information con-
cerning the relative proportion of the various constituents,
they give a means of expressing, in a precise manner, the
dimension of the grain, which seems to be the best character-
istic of the conditions in which solidification has been effected.

II. Eutectic Alloys.*

The constitution of *eutectic* alloys, or alloys with the *lowest
melting-point*, was one of the most interesting questions to be
studied through microscopic examination. The property to
melt at a temperature lower than all other mixtures of the
same substances has long been considered as a characteristic
of a definite compound. This preconceived idea seems even
to have led certain investigators to accept inaccurate results
concerning the composition of those alloys. So it is that
Rudberg indicates that the most fusible alloy of tin and bis-
muth corresponds to the formula Sn_3Bi_2, which melts at
143° C., while, as a matter of fact, according to Guthrie, the
most fusible alloy melts at 133° and contains 46.1 per cent of
bismuth instead of 45.74 per cent required by the formula
Sn_3Bi_2.

The fact that the composition of eutectic alloys cannot,
in general, be expressed by simple multiples of atomic weights
has been conclusively established by Dr. Guthrie in a series
of memoirs published in the *Philosophical Magazine* from 1875
to 1884. We shall quote here a few passages of his last
article, entitled : "On Eutexia" (*Philosophical Magazine*,
June, 1884) :

". . . The eutectic alloys of metals, many of which have been long
imperfectly known, and the eutectic alloys of salts, which I shall describe,
are the perfect homologues of the cryohydrates.

"The statement, therefore, that alloys of minimum melting-points
are got on mixing the metals in certain simple ratios of their atomic
weights is presumably to be put on one side. As the cryohydrate forms
itself when a salt-solution of any strength loses heat, so the eutectic alloy
forms itself when an alloy whose constituents are in any ratio is cooled.

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* See Professor Roberts-Austen's lecture on alloys in the present
number of *The Metallographist*. Also Vol. I. No. 1 (January, 1898), page
19 and seq., Mr. Osmond on eutectic alloys; and page 59 and seq., Mr. H.
Le Chatelier on the same subject. — ED.

"That certain metals may and do unite with one another in the small multiples of their combining weights may be conceded. To such bodies the eutectic alloys bear the same relationship as the cryohydrates bear to the common hydrates, and, like the latter bodies, their constituents are not in the ratio of any simple multiples of their chemical equivalents. But their composition is not, on that account, the less fixed, nor are their properties the less definite.

"Firstly, as a salt may unite with water, as when anhydrous chloride of calcium does so, to fix the water as crystalline water, and also may unite with water as a cryohydrate, so two metals may unite in one proportion while they form a definite eutectic in another. Secondly, the very bodies resulting from the chemical union of the two metals will possibly, and probably, furnish starting-points of new series of eutectic alloys, consisting of a simple metal on the one hand, and the chemical alloy on the other."

We are therefore led, when two metals may be mixed in all proportions, to consider some of these alloys as more especially definite: Some of them are true chemical combinations, being formed with evolution of heat through the union of simple multiples of atomic weights; others, which constitute the portions solidifying last when an alloy is allowed to cool, have a constant composition, but which cannot generally be expressed by a simple formula. The latter may be compared to those solutions which distillate with a constant composition (such as mixtures of hydrochloric acid and water, of alcohol and water, etc.), which phenomenon, as shown by Mr. Berthelot, does not in any way imply the existence of a definite compound.

What, then, is the composition of these eutectic mixtures? Are they chemical combinations of a peculiar character or homogeneous mixtures, sorts of solid solutions which might be compared to glass: or else, are they heterogeneous mixtures in which the two substances exist in close contact in an extreme state of division? Various researches have been undertaken in order to elucidate this question. Mr. Offer has shown in 1880 that the cryohydrates, i.e., the mixtures of aqueous saline solutions, never form well-defined and transparent crystals, but opaque masses: that alcohol dissolves the ice and leaves a crystalline net-work of solid salt; that the heat of dissolution is equal to the sum of the heats of dissolution of the ice and of the salt: finally, that the specific weight is equal to the mean specific weight of the constituents.

By means of colored salts or by utilizing the phenomena of polarization, Mr. Ponsot ascertained, in 1895, that the cryo-hydrates were made up of juxtaposited crystals alternately of ice and of solid salt, the latter anhydrous or hydrated.

These experiments seem to demonstrate clearly that the eutectic mixtures are heterogeneous mixtures.

The microscopic study of the eutectic alloys of metals has given us results identical to those of Mr. Ponsot regarding the cryohydrates. The eutectic alloy of tin and bismuth was first examined. 200 grammes of the alloy was prepared by melting together some tin and some bismuth in the proportions indicated by Mr. Guthrie, i.e., 46.1 per cent of bismuth and 53.9 per cent of tin. It was allowed to cool slowly from the molten condition; when most of it had solidified, the portion remaining liquid, and which possessed exactly the composition of the eutectic alloy, was decanted. This portion, after solidifying, was the one used for the study of the structure.

The examination of a polished surface, etched with very dilute hydrochloric acid which dissolves the tin only, shows that the two metals are simply juxtaposited; the crystals are extremely minute, requiring relatively large magnifications to be clearly distinguished. Fig. 1 (Frontispiece) shows a photomicrograph of one of these preparations magnified 200 diameters; the black portions indicate the bismuth, the white areas the tin which was dug out by the acid. This figure is a negative of the true appearance of the preparation, it having been found that, in this case, a negative print was better suited to reproduction. It is seen that some portions of the surface are made up of white grains, while others reveal a striated structure in black and white. This appearance is produced only when the solidification has taken place very slowly; if the metal be suddenly cooled, the whole surface is uniformly striated, but the crystals are then so small that it is very difficult to obtain satisfactory photographs. It would seem that during slow cooling a first separation takes place of portions rich in bismuth and of portions rich in tin, the metals separating subsequently in each of these portions in the shape of thin plates or lamellæ. In the parts appearing white in the photograph there are indeed very fine

brilliant striæ which have nearly disappeared in the repro-
duction. This very finely laminated structure seems to be
characteristic of eutectic alloys. We have found it in every
case which has been examined; it is always perfectly distinct
in the portions of alloys solidifying last, and surrounding
crystals of some pure metal or of some definite compound.

Fig. 2 (Frontispiece) shows an alloy containing 66 per
cent of silver and 34 per cent of antimony, magnified 500
diameters; the preparation has been treated with hydro-
sulphuric acid, which darkens the silver while it has no action
on the antimony. This figure was also reproduced from a
negative print, so that here the silver appears white. The
alloy is made up of large areas of silver surrounded by the
eutectic alloy which clearly exhibits the alternate layers of
silver and antimony.

Instances of such splitting up of eutectic alloys will not be
multiplied here, as we shall meet them repeatedly farther on.

Eutectic alloys, therefore, whose composition is perfectly
known, exist in the solid state as simple mixtures of their
constituents. The very minute division of these components
is sufficient to impart to them special properties; it may be
conceived, for instance, why in a number of cases they exhibit
a conchoidal fracture, which would lead, at first sight, to con-
sider them as homogeneous bodies.

We have found the same characteristics in the mixtures
of melted salts, which may be ground down to very thin
plates, one or two tenths of a millimeter in thickness, and
then examined as transparent objects. In most cases, trans-
parent crystals are detected, surrounded by a mixture which
is relatively opaque, owing to the refraction-phenomena pro-
duced by the very tenuous crystals of which it is composed.
These small crystals may be distinguished, under high mag-
nifications, in the thinnest portions of the preparation.

III. Alloys with Normal Curves of Fusibility.

According to Mr. H. Le Chatelier, the normal curves of
fusibility of binary mixtures may be grouped according to
three types: (1) two branches of curves starting from the
melting-points of the pure metals and meeting at a point cor-

responding to the eutectic alloy; this curve is obtained when
the two metals form neither definite combinations, nor iso-
morphous mixtures; (2) three branches of curves, two of
them starting from the melting-points of the pure metals, and
a third exhibiting a maximum and crossing the former two in
two points corresponding to two eutectic alloys; it is the
case of two metals forming a definite combination; (3) the
curve of fusibility is continuous and unites the melting-points
of the two metals; it is the case of two metals forming iso-
morphous mixtures.

Alloys whose curves of fusibility corresponded exactly to
the three normal types were first examined, namely:

In the *first group*, alloys of tin and bismuth, of lead and
antimony, of lead and tin, of zinc and aluminium.

In the *second group*, alloys of copper and antimony, of
nickel and tin.

In the *third group*, alloys of bismuth and antimony.

Alloys of Lead and Antimony. — The curve of fusibility,
determined by Mr. Roland-Gosselin, is composed of two
branches meeting at a sharp angle and corresponding to the
alloy containing 13 per cent of antimony, from which it is
inferred that the metals are merely in close contact.   Mr.
Laurie, on the other hand, finds that the electro-motive forces
of these alloys vary in a continuous manner with the com-
position, which would lead to suppose that the metals crystal-
lize together.

The microscopical examination clearly confirms the
inference drawn from the curve of fusibility.

In the case of alloys containing 13 per cent of antimony,
hard crystals of antimony are found, surrounded by a eutectic
alloy whose splitting up becomes visible after a weak attack
with nitric acid.   Figs. 5, 6 and 7 exhibit the appearance,
magnified 200 diameters, of alloys containing respectively
about 70, 40 and 20 per cent of antimony, and photographed
after having been polished and without further treatment.

Alloys containing from 0 to 13 per cent of antimony pre-
sent an entirely different aspect; they are difficult to polish,
but large dendrites are easily detected, which blacken when
the surface is treated with sulphuretted hydrogen; they are
soluble in nitric acid and are surrounded by a eutectic alloy.

The proportion of these dendrites, probably composed of pure lead, varies as the amount of lead present. The appearance of such alloys is entirely similar to that of Fig. 8.

It seems evident, therefore, that when an alloy containing less than 13 per cent of antimony is allowed to cool slowly, as soon as the beginning of solidification is reached, crystallites of lead are formed resembling fern-leaves which gradually grow as the temperature falls; when the portion remaining liquid has reached the composition corresponding to the eutectic alloy, it solidifies in bulk, the lead and the antimony

FIG. 5. Alloy of Lead and Antimony.
70 per cent antimony.
Magnified 200 diameters.

FIG. 6. Alloy of Lead and Antimony.
40 per cent antimony.
Magnified 200 diameters.

being then deposited simultaneously as very thin crystallitic plates. When an alloy containing more than 13 per cent of antimony is slowly cooled, a similar phenomenon takes place, but it is then the antimony which solidifies until the remaining liquid has reached the composition of the eutectic alloy.

Alloys of Lead and Tin, of Zinc and Aluminium. — The fusibility-curves of these alloys are also made up of two branches meeting at points corresponding respectively to the alloys containing lead 35 per cent, tin 65 per cent, and aluminium 5 per cent, zinc 95 per cent.

The microscopical examination yields results similar to those indicated in the case of lead and antimony. As all the constituent metals are relatively soft, the polishing operation is difficult and does n●t place in relief any of the components.

In the case of alloys of lead and tin, hydrochloric acid dissolves the tin while the lead is covered with a white layer of chloride. Nitric acid, on the contrary, dissolves the lead and covers the tin with a layer of white metastannic acid. The appearance of the preparation is therefore the reverse, when treated with hydrochloric acid, from what it is when

FIG. 7. Alloy of Lead and Antimony.
20 per cent antimony. Magnified 200 diameters.

etched with nitric acid. It is not possible to prepare a surface that will permit the use of high magnifications, and the latter are required to resolve the eutectic alloy.

·In the case of zinc and aluminium, a somewhat diluted solution of caustic potash leaves the zinc nearly unaffected while it rapidly dissolves the aluminium, producing cavities which appear black under the microscope. The zinc is present in the form of radiating crystals, often as six-pointed stars in alloys containing little zinc; aluminium crystallizes in dendritic needles.

Alloys of Tin and Bismuth. — These alloys belong to the same group and are better adapted to photographic reproduction. The structure of the eutectic alloy of these metals has been shown in Fig. 1 (Frontispiece). Figs. 8 and 9 exhibit the appearance of mixtures containing respectively about 20 and 60 per cent of bismuth, etched with hydrochloric acid. In the first instance, the eutectic alloy, whose laminated structure may be distinguished, surrounds dendrites of tin which have been dug out by the acid and appear black; in the second case the eutectic alloy surrounds some white crystals of antimony which were already discernible after polishing.

Alloys of Iron and Carbon. — The microstructure of alloys of iron and carbon — especially of steel — has been the object of numerous researches, ever since Dr. Sorby created microscopic metallography by applying it to the study of these metals. It may be interesting, nevertheless, to compare some of the acquired facts with those that we have just described.

When the most recent researches, those of Messrs. Osmond, Arnold and Sauveur, are compared, it is seen that they practically agree concerning the nature of the constituents of steel in its normal condition, i.e., cooled from a high temperature sufficiently slow to allow the various transformations of iron and carbon to take place in their integrality. Three constituents are then found, if we omit the graphite, which appears only under special conditions, and the forms of transition which, strictly speaking, are not constituents; they are:[*]

1. *Ferrite*, composed of nearly pure iron.

2. *Cementite*, a carbide of iron corresponding to the formula Fe_8C.

3. *Pearlyte*, a constituent answering to the formula $Fe_{24}C$, i.e., containing 0.89 per cent of carbon, but which under the microscope is seen to be made up of plates, alternately of ferrite and cementite.[†]

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[*] The microstructure of steel has been described at length in Vol. I. No. 1 of *The Metallographist* (January, 1898), page 19 and seq., and page 30 and seq. — ED.

[†] See Frontispiece *loc. cit.* — ED.

When the steel contains less than 0.89 per cent of carbon, it is formed of ferrite and pearlyte ; when it contains more than that amount of carbon, it is formed of pearlyte and cementite.*

When it is noticed that the structure of pearlyte is identical to that of eutectic alloys, being like them made up of alternate layers of two different constituents, the analogy between the constitution of steel and that of alloys like those of tin and bismuth, for instance, appears striking ; steel is

FIG. 8.   Alloy of Tin and Bismuth.
20 per cent bismuth.

FIG. 9.   Alloy of Tin and Bismuth.
60 per cent bismuth.

composed of iron and the carbide Fe_3C, just as the latter alloys are composed of tin and bismuth, pearlyte correspond-

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* When the metal is made up entirely of pearlyte, it is said to be saturated. Professor Arnold found that in the case of steel containing *very little* impurities the saturation-point corresponds to 0.89 per cent of carbon — that such, therefore, is the carbon-content of pearlyte. In commercial steel, however, containing about 1 per cent of impurities besides carbon, 0.80 per cent of carbon is sufficient to saturate it. The pearlyte of commercial steel of that grade, then, contains in the neighborhood of 0.80 per cent of carbon, and may contain much less carbon, in the case of a more impure metal, especially if considerable manganese be present. See *loc. cit.*, page 33 and seq. — ED.

ing to the eutectic alloy. The only conclusion I wish to draw from the above considerations is that there is no reason to consider the alloy containing 0.89 per cent of carbon as a definite compound, as was recently proposed by Prof. Arnold. All the properties invoked for that purpose are to be found in alloys formed of simple mixtures when the eutectic alloy is reached; to the latter correspond critical points in all the properties, but, as we have seen, it does not by any means follow that this is a definite compound.

Alloys of Antimony and Copper. — The curve of fusibility of these alloys, determined by Mr. H. Le Chatelier, is composed of three branches crossing each other at two points corresponding to the alloys containing respectively about 25 and 71 per cent of copper; the intermediate branch exhibits a maximum at about 60 per cent of copper. This leads to admit the existence of a definite compound answering to the formula $SbCu_2$, for which composition the electric conductivity, ascertained by Mr. Mathiessen, also reaches a maximum.

The microscopical examination confirms the existence of this compound, and shows that these copper alloys may be classified in four very distinct groups.

The *first group* includes alloys containing from 0 to 25 per cent of copper. After polishing, hard crystals of antimony are seen, surrounded by a eutectic alloy. The structure is distinctly revealed through an etching with diluted hydrochloric acid. Fig. 10 shows the appearance of the structure of an alloy containing 10 per cent of copper and magnified 60 diameters. The white portions are made up of crystals of antimony; the eutectic alloy appears entirely black, because the etching was somewhat prolonged. A high magnification, however, reveals the presence of two juxtaposited elements. As the proportion of antimony increases from 0 to 25 per cent, the crystals of antimony decrease gradually, without, however, any alteration in their forms, precisely as in the case of alloys of lead and antimony described in the foregoing pages.

The *second group* includes alloys containing from 25 to 60 per cent of copper, which, upon being examined after polishing, are seen to be made up of crystallites of a distinct violet color, surrounded by a eutectic alloy appearing nearly white,

when moderately magnified, and which splits up into two elements, especially when the preparation has been etched with hydrochloric acid and heated in the atmosphere, so as to induce a slight oxidation. The violet-colored crystallites increase in quantity as the amount of copper increases, forming the totality of the alloy when the latter contains 60 per cent of copper. These alloys cannot be easily photographed for want of sharpness on the sensitive film between the violet color of the crystal and the white color of the matrix. Fig. 11 shows the structure of an alloy containing 40 per cent of

FIG 10.   Alloy of Copper and Antimony.
10 per cent copper.
Magnified 60 diameters.

FIG. 11.   Alloy of Copper and Antimony.
40 per cent copper.
Magnified 60 diameters.

copper and magnified 60 diameters, after an etching of sufficient duration to cause the crystallites to stand in relief; they are indicated by the white areas in the reproduction. The composite structure of the surrounding eutectic alloy may be detected under a moderate enlargement.

The *third group* includes alloys containing from 60 to 70 per cent of copper. Their polished surfaces exhibit a uniform violet tint, but under the microscope, violet-colored crystalline grains are detected, surrounded by a net-work of a white substance made up of small crystals which sometimes penetrate

into the interior of the grains. When the metal is heated, the substance forming the net-work is oxidized first. Fig. 10 shows the appearance of an alloy containing 65 per cent of copper, magnified 100 diameters. The lighter portions correspond to the violet grains; a few fragments of the substance which composed the net-work, and which corresponds probably to the second eutectic alloy, may be detected in the interior of the grains. Such structure, made up of crystalline grains, is met with quite frequently in alloys, notably in alloys of copper and aluminium containing 10 per cent of aluminium, in alloys of copper and tin with 25 per cent of tin, of copper and zinc with 50 per cent of zinc. Their structure is similar to that shown in Fig. 3 (Frontispiece).

The *fourth group* includes alloys containing over 70 per cent of copper. Polishing alone does not reveal their structure, but upon being heated some crystallites are first oxidized which appear to be surrounded by a eutectic alloy. These crystallites unite to form long dendritic threads which are the closer together, the larger the amount of copper present. Fig. 4 (Frontispiece) exhibits the appearance of the structure of an alloy containing 85 per cent of copper and magnified 30 diameters. The dark areas sharply outlined are probably made up of pure copper, the light portions corresponding to the eutectic alloy.

From the above considerations the constitution of alloys of copper and antimony may be explained as follows: in the case of alloys containing less than 25 per cent of copper, pure crystals of antimony are separated when solidification begins, increasing gradually in size as the temperature decreases; the portion remaining liquid, therefore, gradually becomes richer in copper until the composition of the eutectic alloy is reached; it then solidifies, at a constant temperature, through a simultaneous crystallization of antimony and $SbCu_2$. In the case of alloys containing from 25 to 60 per cent of copper, a similar phenomenon occurs, only it is the definite compound $SbCu_2$ which separates from the molten mass as soon as the freezing-point is reached. When from 60 to 70 per cent of copper is present, the same compound is separated, but is in this case surrounded by a second eutectic alloy made up of copper and the compound $SbCu_2$. Finally, when more than

they seem to point strongly to allotropy as contributing to the hardening.

Mr. Hadfield, however, thought that stress might account for much of this.

To get further light, especially on the question of stress, I have made the experiments which I will now describe. Several small bars of basic open-hearth steel, made under the direction of Superintendent H. H. Campbell, of the Pennsylvania Steel Company, and containing carbon, 0.04 per cent; silicon, trace; manganese, 0.03; phosphorus, 0.007; sulphur, 0.014, and copper, 0.10 per cent, all machined out of the same block of this steel, were treated as is shown in the following table:

Hardening of Steel of 0.04 % of Carbon (Series 29).

No.	Size. Inches.	Bored or not.	Size of holes bored. Inches.	Tenacity lbs. per square inch.	Elastic limit lbs. per square inch.	Elongation per cent in 1 inch.	Contraction of area, per cent.	Treatment.
6	.162×.174	Not	—	48,580	23,050	44.	72.3	} Cooled slowly
10	.187×.204	Yes	.083×.082	49,890	—	—	—	from 930° C.
2	.176×.181	Not	—	52,040	30,400	34.	77.8	{ Quenched in water from 930° C.
9	.183×.198	Not	—	67,400	42,820	28.	58.56	Quenched in iced brine from 930° C.
3	.177×.186	Yes	.073×.074	70,690	—	—	—	
7	.178×.197	Yes	.086×.085	60,190	—	—	—	
8	.179×.195	Yes	.087×.088	62,450	—	—	—	

These bars were machined out of a solid block of this steel, were heated approximately to 930° C., in a double-walled copper muffle. Only very little scale was formed. The subsequent cooling was extremely slow, occupying several hours, as the bars were allowed to cool down in the furnace. While drilling the bars, I sprayed them with rhigolene to prevent them from heating.

The properties of the slowly cooled bar No. 6 are such as we should expect this material to possess in its normal state, and are confirmed by those of bar 10. Comparing it with bar 9, which was quenched in iced brine, we see that sudden cooling has apparently raised the tenacity by 39 per cent and the elastic limit by 86 per cent. These results appear to me too great to be referred to any direct action of the minute quantity of the foreign elements present. The two other causes thus far suggested are allotropy and stress.

I next proceeded to learn how far this result could be attributed to stress, by quenching bars 3, 7 and 8 in the same way, in iced brine, and then removing their interiors by drilling two transverse holes across each of them, the axes of the two holes intersecting, so that the remaining section consisted of four small rectangles, one at each of the four corners of the bar. This removal of the interior should greatly relieve the stress; nevertheless we find that these bars still show a great increase of tenacity, bar 3 thus drilled out being actually stronger than bar 9, which had not been drilled out, and 45 per cent stronger than slowly cooled bar 6. Hence I infer that stress is probably not an important cause of the strengthening here observed, especially as the strongest bar of all is one which should have relatively little stress, and as in a previous experiment I found that the stress in a quenched bar of 0.39 carbon-steel seemed to be a source not of strength but of weakness. The strengthening of these bars may thus be rather in spite of stress than because of it.

While the variations of tenacity between these three bars, 3, 7 and 8, are readily understood, all four of the quenched bars unite in having far greater tenacity than the slowly cooled bars.

To show further that the great strength of the quenched and drilled bars is not due to their peculiar section as such, I cooled bar 10 slowly, and then drilled out its interior in the same way. This has not affected its tenacity materially.

It may be possible that these effects are due jointly to the direct action of the foreign elements so sparingly present, and to stress and other causes yet unsuggested. But it seems to me as difficult to explain them in this way as it is easy to explain them by supposing that the allotropic iron, shown by wholly independent evidence to form at high temperatures, has been in part retained by the rapid cooling, and that it is stronger but less ductile, with higher elastic limit, than iron in the normal state reached by slow cooling.—*The Engineering and Mining Journal*, December 12th, 1896.

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In the issue of *The Engineering and Mining Journal* for December 12th, 1896, I gave results showing that the tenacity

of steel containing * only 0.022 per cent of carbon, no manga-
nese, silicon trace, phosphorus 0.007 per cent, sulphur 0.014
per cent, and copper 0.10 per cent, could be increased 39 per
cent, and its elastic limit raised 86 per cent, by rapid cooling.
Since then I have obtained still more remarkable results with
this same steel in the form of wire. On quenching it in iced
brine, I raised its tenacity by no less than 132 per cent, from
an average of 49,235 lbs. per square inch to 114,000 lbs. per
square inch, and I lowered its elongation by some 63 per
cent, from 44 per cent in 1 in. to 16 per cent in 3 in.

It has been suggested by Mr. Hadfield that the strength-
ening of this low-carbon steel by sudden cooling may be due
to stress, or, as he terms it, " surface tension." He intimated
his intention to quench a bar of very low-carbon steel or iron
and then machine it " to remove the surface tension induced
by sudden cooling." He thought "it was probable the result
would show but little gain in tenacity." I gave results in
the article to which I have just referred, tending to show that
this strengthening of this almost carbonless iron is not to be
referred to stress. I have now carried out the experiment
which Mr. Hadfield above outlines, by quenching a bar of
this same steel 0.1770 in. $\times$ 0.225 in., turned down for a short
distance in its middle to a diameter of 0.1717 in.

After quenching it, I then turned it down still farther,
to a diameter of 0.112 in., and found that the remaining
cylinder, which thus represented the central core of the bar,
was hardened even more than the average section of such a
bar taken whole. Its tenacity was 72,400 lbs. per square
inch, and its elongation 18 per cent in 1 in. A nearly like
bar, quenched under like conditions, and tested as a whole,·
that is without having any part cut away after quenching,
had a tenacity of only 67,400 lbs. per square inch and 28 per
cent elongation in 1 in. The greater hardening which I here
find in the core may be due to the slight variations in con-

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* In describing my earlier results in the issue of December 12th,
1896, I reported the carbon as 0.04 per cent and the manganese as 0.03.
These were the numbers furnished me by the makers of the steel. The
carbon and the manganese have since been determined, the former by
combustion, by Booth, Garrett & Blair, with the results which I give
above, carbon, 0.022 per cent ; manganese, zero.

ditions, and I purpose to ascertain by further tests whether it is. It has occurred to me that the great pressure in the interior of the bar may retard the change of the iron from the allotropic to the normal state. M. Moissan has found that, under like conditions, such pressure suffices to prevent the diamond from passing back allotropically to graphite during sudden cooling. As the central core must cool less suddenly than the average of the whole, some special compensating cause must be at work if the inside hardens more than the outside. I found this same result in earlier experiments with other steel higher in carbon. — *The Engineering and Mining Journal*, January 30th, 1897.

ON page 111 of *The Engineering and Mining Journal* for January 29th, 1897, I gave the tenacity of hardened steel wire, containing only 0.022 per cent of carbon, as 114,000 lbs. per square inch. I gave this on the strength of the report of a trustworthy public testing company on the tensile test of a wire which I hardened and sent it. On repeating the experiment, the highest tenacity which I find is 66,154 lbs. in a very short fragment of number 13 specimen; 63,476 lbs. in a longer piece, and 91,800 lbs. in a fragment of a quenched wire which had already been tested. On investigating the matter I find that the tenacity of 114,000 lbs. originally given to me was wrong, and was due to an error in calculation made by that testing company. — *The Engineering and Mining Journal*, July 3d, 1897.

ON THE DETERMINATION OF HARDENING CARBON AND CARBIDE CARBON.*

By H. JÜPTNER VON JONSTORFF.

IT is hardly necessary to point out the importance, both from scientific and practical points of view, of having methods available for rapidly and simply quantitatively determining the various forms of carbon. As, however, methods of this kind have unfortunately hitherto been want-

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ing, the author has endeavored to supply the deficiency, and decided, after various researches in other directions, to investigate whether the colorimetric method originally introduced by Eggertz would, if modified, be adapted for the determination of the different forms of " combined " carbon.

In recording in this paper the results of this investigation, the author cannot refrain from pointing out that in colorimetric determinations absolute accuracy can obviously not be expected. In the comparison of color intensities an error of $\pm$ 5 per cent must be reckoned with, and moreover, with the small quantities which are used in practice, and with the various kinds of operations, other sources of error are introduced.

In the first place, it may not be out of place to give a short review of our present knowledge of the subject. As is well known, there are now distinguished in iron and steel at least four different forms of carbon, which have the following characteristics :

a. Hardening Carbon. — On dissolving in dilute hydrochloric or sulphuric acid this is given off as strongly smelling carburetted hydrogen gas. On dissolving in cold nitric acid of 1.2 specific gravity it forms at first a dense black residue, which dissolves very rapidly on shaking or at rest in a few minutes, without noticeable evolution of gas, and on heating the solution to 100° C. is gradually given off in the form of gas, the solution colored dark by the dissolved carbon compounds becoming increasingly lighter in color.

β. Ordinary Carbide Carbon. [Cement Carbon. — ED.] — On heating with strong acids this modification is given off in the form of carburetted hydrogen. If the sample of metal is dissolved in very dilute hydrochloric or nitric acid at ordinary temperature, a grey or brown mass (carbide) is left, which, according to Müller, consists of a number of silvery granules which when dried catch fire at a comparatively low temperature. According to F. Mylius, F. Förster, and G. Schoene, this carbide is decomposed even by the most dilute acids, and in a wet condition is oxidized by the oxygen of the air. On dissolving the sample of iron in cold dilute nitric acid of 1.2 specific gravity, it remains as a flocculent brown mass, which on heating gradually dissolves without evolution of gas, and

imparts to the solution a brown color which changes but little, even on boiling.

γ. *Graphitic Temper Carbon* is neither soluble even in boiling acids nor volatilized. It remains in the residue as almost pure carbon. It is black, without lustre, and perfectly amorphous, and can, by ignition under oxidizing influences, be entirely removed from iron, according to Forquignon, even by igniting in a current of dry hydrogen, in this case of course as carburetted hydrogen.

δ. *Graphite* behaves towards acids in the same way as temper carbon, from which it is distinguished only by the crystallization. It is usually assumed that graphite is not acted upon by boiling nitric acid. This is however incorrect, as it is oxidized slowly but completely, a reaction which I have utilized for many years past in the determination by the chlorate method of manganese in grey pig iron. Temper carbon behaves in a similar manner.

The methods hitherto employed for the quantitative determination of the various forms of carbon are briefly as follows :

1. Temper carbon and graphite, which cannot as yet chemically be separated, are best obtained by dissolving the sample in nitric acid, collecting on a filter, and determining in the usual manner.

2. The difference between the total carbon and the proportion of graphite and temper carbon found, according to 1, gives the so-called " combined carbon," which may, however, also be determined colorimetrically by the methods of Eggertz and Stead. These methods present the disadvantage that they are perfectly trustworthy only when the different modifications of combined carbon in the sample and in the normal steel are in similar proportions.

3. The separation of the carbide carbon from the iron is based on its insolubility in dilute cold acids; it is deposited in the form of a greyish black powder. Pure iron, on the other hand, and iron uniformly alloyed with a little carbon, is dissolved to a clear solution, the carbon being evolved in the form of carburetted hydrogen. Whilst Müller employed dilute sulphuric acid, Sir Frederick Abel and Deering used a mixture containing in one liter 100 grammes of potassium

bichromate and 90 grammes of sulphuric acid. The method introduced by F. C. G. Müller is as follows: For every gramme of the sample, comminuted as much as possible, 20 cubic centimeters of 10 per cent sulphuric acid is added, and the beaker containing the mixture is placed under a bell-jar through which a quite slow current of illuminating gas is allowed to flow. In a few days' time the action of the acid is complete. The residue is filtered off on to a weighed filter, washed with a large quantity of boiling water, and finally with a mixture of ether and alcohol. The filter and its contents are then placed in a weighing bottle in an air bath at 120°C., care being taken to pass illuminating gas slowly through it by means of a cork with two holes bored in it. After drying it is allowed to thoroughly cool in the current of gas. The substance is so inflammable that it always ignites spontaneously if the glass is even just warm. When it is merely a question of determining the carbide carbon and not of isolating the carbide itself, the course of procedure is to filter over asbestos instead of through a paper filter, wash free from iron with water, then with ether and alcohol (which according to Ledebur may be dispensed with), finally with water again, and determine the separated carbon by one of the known methods as carbonic anhydride. Mylius, Förster, and Schoene found that the carbide is least attacked by dilute acetic acid. The solution of the iron in this acid occupies, however, much too long a time for it to be of practical use.

4. Hardening carbon has not hitherto been determined directly. It is obtained by subtracting from the proportion of total carbon those of the other forms of carbon. In this way all the errors occurring in the other determinations are accumulated, so that the result is by no means free from error.

Description.	A.	B.	C.	D.
	Per cent.	Per cent.	Per cent.	Per cent.
Temper carbon	—	0.17	—	—
Carbide carbon	0.64	0.90	0.71	0.38
Hardening carbon	0.14	0.13	0.22	0.55
Total carbon	0.78	1.20	0.93	0.93
Silicon	0.37	0.79	0.11	0.11
Manganese	0.26	0.40	0.11	0.11
Phosphorus	0.01	0.07	0.03	—

Consequently it is undoubtedly a considerable advantage that the new methods enable the hardening carbon to be determined directly.

The following experiments are based on four samples of steel, kindly supplied by Professor A. Ledebur, of Freiberg. Their composition is shown in the table on page 157.

In addition, other samples of steel were used whose total carbon contents had been carefully determined.

No.	Sample.	Hardening Carbon. Per cent.		Difference.
		Colori-metri-cally.	Gravi-metri-cally.	
1	A	0.14	0.14	0.00
2	A	0.14	0.14	0.00
3	A	0.135	0.14	—0.005
4	A	0.135	0.14	—0.005
5	A	0.143	0.14	+0.003
6	A	0.138	0.14	—0.002
7	A	0.138	0.14	—0.002
8	A	0.148	0.14	+0.008
		Mean 0.140	Mean 0.14	Mean 0.000
9	B	0.138	0.13	+0.008
10	B	0.105	0.13	—0.025
11	B	0.140	0.13	+0.010
12	B	0.133	0.13	+0.003
13	B	0.136	0.13	+0.006
14	B	0.133	0.13	+0.003
15	B	0.120	0.13	—0.010
16	B	0.120	0.13	—0.010
		Mean 0.128	Mean 0.13	Mean — 0.002
17	C	0.222	0.22	+0.002
18	C	0.220	0.22	0.000
19	C	0.230	0.22	+0.010
20	C	0.199	0.22	—0.021
21	C	0.200	0.22	—0.020
22	C	0.219	0.22	—0.001
23	C	0.222	0.22	+0.002
24	C	0.242	0.22	+0.022
25	C	0.202	0.22	—0.018
26	C	0.220	0.22	+0.000
		Mean 0.218	Mean 0.22	Mean —0.002

(*a*) *Determination of the Hardening Carbon by Solution in Dilute Nitric Acid in the Cold.* — Usually 0.2 gramme of the sample was weighed out, and on this 10 cubic centimeters of nitric acid was poured, the sample being placed in a vessel containing cold water and dissolved, shaking frequently. The nitric acid used consisted of two parts by volume of concentrated acid and three of water. It was then filtered through a dry filter, hardened with nitric acid, 2 cubic centimeters of the filtrate transferred to a comparing tube, and diluted until it was of the same color as the solution of the standard steel. In these tests those samples of steel containing but little hardening carbon — under 0.15 per cent — showed a distinct greenish coloration, with a result that the color comparison was difficult to effect. The greenish color tint causes the solutions to appear far lighter in color than should correspond to the carbon percentage. Numerous experiments showed,

however, that the results are satisfactorily in accord if the value of the hardening carbon of the normal solution as determined for brownish-colored solutions was multiplied by 1.3 for solutions of a greenish tint. In this way, for instance, the values shown on the opposite page were obtained.

(*b*) *Change in Color in the Cold Solution of Hardening Carbon after Long Standing.* — After long standing at the ordinary temperature the solution of hardening carbon becomes paler. The absolute amount of hardening carbon decomposed after standing for twenty-four hours was:

> In sample A . . 0.14 × 0.167 = 0.02338 per cent of carbon.
> ,, B . . 0.13 × 0.219 = 0.02847 ,, ,,
> ,, C . . 0.22 × 0.069 = 0.02518 ,, ,, .
> ,, F . . 0.09 × 0.276 = 0.02484 ,, ,,

(*c*) *Change of Color of the Solution of Hardening Carbon with Increasing Temperature.* — Even on heating to 80° C. the solution becomes paler, the effect being the greater the longer the heating lasts.

For the same duration of heating the decrease in coloring, that is to say the loss of carbon, appears to increase with the amount of hardening carbon present.

(*d*) *Determination of the Hardening Carbon at* 80°. — The determination of the hardening carbon may also be effected by dissolving the steel in dilute nitric acid in the cold, filtering after the evolution of gas has ceased, through a dry filter paper hardened in nitric acid, and then an aliquot portion of the filtrate, after being heated to 80°, used for the color comparison. Of course all the samples to be compared must be heated for the same time and to the same temperature, as they would otherwise not be comparable, as previously mentioned. In this way, using 0.2 gramme samples, and 10 cubic centimeters of dilute acid in the solution of the samples, the following values were obtained, and 2 cubic centimeters of the hardening carbon solution being employed in comparing the color intensities.

One cubic centimeter of the solution, subjected to comparison, corresponds, after heating for about thirty minutes to 80° C., to the following quantities of hardening carbon:

Samples.	Series of Experiments.		
	1.	2.	3.
	Milligrammes.	Milligrammes.	Milligrammes.
A.	0.01914	0.02800	0.02545
B.	0.01793	0.02737	0.02261
C.	0.01796	0.02933	0.02750
Averages . .	0.01834	0.02823	0.02519

(*e*) *Determination of the Hardening Carbon and Carbide Carbon Contents in Steel.* — For the determination of the hardening carbon 0.2 gramme of steel is taken, and dissolved in dilute nitric acid in the cold — 2 volumes of concentrated acid and 3 of water — that is to say, by placing the dissolving vessel in cold water. The solution is well shaken repeatedly, and when no further evolution of gas can be observed, it is well mixed and filtered through a dry filter without subsequent washing. Two cubic centimeters of the filtrate are used for the determination of the hardening carbon by direct comparison with the normal solution, and another 2 cubic centimeters placed for the time on one side.

In the meantime, for the determination of the carbide carbon, 0.04 gramme of the sample of steel under examination is weighed out for each test, 10 cubic centimeters of the dilute nitric acid, described above, poured on to it, and then transferred to a water-bath at 80°, *simultaneously* with the other 2 cubic centimeters tests solution for hardening carbon which had been placed on one side, as previously mentioned. As soon as complete solution is effected, both series of solutions are compared with the same standard solution, and from the compared volume of the solution of the total carbon, the compared volume of the hardening carbon solution which had been heated to 80° is subtracted. The difference gives the volume corresponding to the carbide carbon, and from this the percentage contents can be readily calculated.

For the purpose of this comparison I use unchangeable empirical standard solutions, consisting of slightly acidulated solutions of Fe_2Cl_6 and $CoCl_2$. If it is desired to obtain as great a degree of accuracy as possible, two such solutions can be employed, differing but slightly from each other in their tints.

Should the small tubes used in comparing the colors of the solutions not be of exactly the same width, which may be ascertained by comparing the lengths of their subdivisions, a volume correction may be readily made when it is remembered that the color intensity of one and the same solution is directly proportional to the square of the thickness of the layers of solution, and therefore inversely proportional to the height of the columns of liquid under comparison.

One series of experiments may be selected from among many others as an example:

(a) *Determination of Hardening. Carbon.* — Quantity of sample taken, 0.2 gramme, dissolved in 10 cubic centimeters of nitric acid and filtered; 2 cubic centimeters of the filtrate was compared in the cold, and 2 cubic centimeters after simultaneous heating to 80° with the Eggertz test for carbide carbon. The comparison made in the cold shows:

	A.	B.	C.	G.
Volume compared . . .	2.0 c.c.	2.2 c.c.	4.0 c.c.	5.6 c.c.
Factor for correction due to unequal width of the calibrated tubes . .	$\frac{47}{40} = 1.175$	$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{1}$
Corrected volume . . .	2.35 c.c.	2.20 c.c.	4.00 c.c.	5.60 c.c.

If steel B be taken as the standard steel, one cubic centimeter of the solutions compared correspond to $\frac{0.13}{2.2} = 0.059$ per cent of hardening carbon, and one obtains:

	A.	B.	C.	G.
	Per cent.	Per cent.	Per cent.	Per cent.
Hardening carbon colorimetrically	0.1387	0.1298	0.2360	0.3304
Difference as comp. with gravimetric method .	— 0.0013	— 0.0002	+ 0.0160	—

The comparison of the 2 cubic centimeters heated to 80° C. showed:

	A.	B.	C.	G.
Volume compared . . .	2.0 c.c.	1.9 c.c.	3.0 c.c.	3.2 c.c.
Factor for correction . .	1.05	0.92	1.00	1.30
Corrected volume . . .	2.10 c.c.	1.73 c.c.	3.00 c.c.	4.16 c.c.

The value of 1 cubic centimeter of the above solutions works out to $\dfrac{0.13}{1.73} = 0.075$ per cent of hardening carbon, and the results are :

	A.	B.	C.	G.
	Per cent.	Per cent.	Per cent.	Per cent.
Hardening carbon colori-metrically	0.1575	0.1298	0.2250	0.3120
Difference as compared with the result by the gravimetric method .	+ 0.0175	— 0.0002	+ 0.0050	—
Average values for the hardening carbon colorimetrically . . .	0.1481	0.1298	0.2310	0.3212
Difference from gravimetric results . . .	+ 0.0081	— 0.0002	+ 0.0110	—

(β) *Determination of the Carbide Carbon.* — Weight of sample taken, 0.4 gramme ; dissolved in 10 cubic centimeters of dilute nitric acid at 80° C., and compared with the normal solution, showed :

	A.	B.	C.	G.
Volume compared (total carbon)	15.3 c.c.	21.5 c.c.	17.9 c.c.	25.8 c.c.
Factor for correction . .	1.00	0.99	1.03	1.02
Corrected volume . . .	15.30 c.c.	21.29 c.c.	18.44 c.c.	26.32 c.c.
Subtracted corrected vol. for hardening carbon	2.10 c.c.	1.73 c.c.	3.00 c.c.	4.16 c.c.
Volume of the carbide carbon solution . .	13.20 c.c.	19.56 c.c.	15.44 c.c.	22.16 c.c.

As the value of 1 cubic centimeter of the carbide carbon solution works out to $\dfrac{0.90}{19.56} = 0.046$ per cent, one obtains :

	A.	B.	C.	G.
	Per cent.	Per cent.	Per cent.	Per cent.
Carbide carbon, colorimetrically	0.6072	0.8998	0.7102	1.0194
Difference as compared with the gravimetric result	— 0.0328	— 0.0002	+ 0.0002	—

Finally, the total percentage of combined carbon is found to be as follows :

	A.	B.	C.	G.
	Per cent.	Per cent.	Per cent.	Per cent.
Hardening carbon (mean)	0.1481	0.1298	0.2310	0.3212
Carbide carbon	0.6072	0.8998	0.7102	1.0194
Combined carbon, colori-metrically	0.7553	1.0296	0.9421	· 1.3406
Combined carbon, gravi-metrically	0.7800	1.0300	0.9300	1.4140
Difference · . .	− 0.0247	− 0.0004	+ 0.0112	− 0.0734

(*f*) *Final Remarks.* — The results recorded show that the determination of the hardening carbon and carbide carbon may be easily and rapidly effected by the colorimetric method with satisfactory results. There are, nevertheless, some points of difficulty connected with the general employment of this method, to which reference must be made. One of the most important sources of error is the liability of the carbide to be attacked by acids, to which Mylius, Förster, and Schoene have recently pointed out. This leads to difficulty, in that it is a somewhat difficult matter to obtain standard steels with percentages of hardening and combined carbon exactly determined.

The solution, too, of the carbide carbon in dilute nitric acid is not constant. The diminution of color is however so slight that allowing to stand even for many hours leads to no error in the result.

It is different, however, with the case of the solutions of hardening carbon. As has been already pointed out, these diminish in intensity of color both on heating and on long standing in the cold, apparently to the greater extent the more hardening carbon is present. But even on dissolving, a portion of the hardening carbon increasing with the percentage appears to escape or at least to be converted into colorless compounds. This, at least, seems to be borne out by the fact that in the examples given under (*e*) the total carbon contents in sample G were found considerably too low — 0.0734 per cent — as it is just this sample which contains

far more hardening carbon — 0.32 per cent — than the others. It appears advisable to use for samples of hardened steel, standard hardened steel of similar composition. This behavior throws fresh light on the ordinary Eggertz test, inasmuch as it affords an explanation of the need of several standard steels, even when the solution is effected at 80° C.

Microscope for the Examination of Metals.* — The accompanying illustration shows a microscope especially constructed for the examination of metals, by the firm of C. REICHERT of Vienna, according to the instructions of Dr. A. REJTÖ of Budapest. In general appearance it resembles the ordinary horse-shoe stand, but it has no mirror, and the stage which is made adjustable in height may also be removed altogether.

With very low powers the specimen may be illuminated by diffused day-light or artificial light, falling freely upon its surface. With higher powers an illuminator is used which fits the tube of the microscope, and is provided with an extension to receive the eye-piece. The illuminator consists of a thin plate of glass placed at an angle of 45° with regard to the axis of the tube, and of a condensing lens whose focal length is equal to the sum of the distances between the lens and the plate of glass, and between the latter and the object.

As source of light the "Auer," a triplex burner, adjustable in height, may be recommended; it is placed at a distance of one meter from the illuminator. The flame is surrounded by an iron or asbestos cylinder with only the necessary aperture for the illumination of the object. The source of light should be at exactly the same level with the lens *b* of the illuminator. On removing the eye-piece and looking through O*c*, it will generally be found that the microscopical field is not evenly illuminated; the light should then be lowered or raised until a perfectly uniform illumination is obtained.

The beam of light received by the lens *b* is made to converge, and is reflected downwards, in the direction of the axis of the instrument, by the glass-plate *a*. It is then condensed

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* *Central-Zeitung für Optik und Mechanik*, No. 17, 1897.

upon the object by the lenses of the objective itself. The illuminated object sends back a portion of the light, which passes through the objective and the plate *a*, reaching the eye at O*c*.
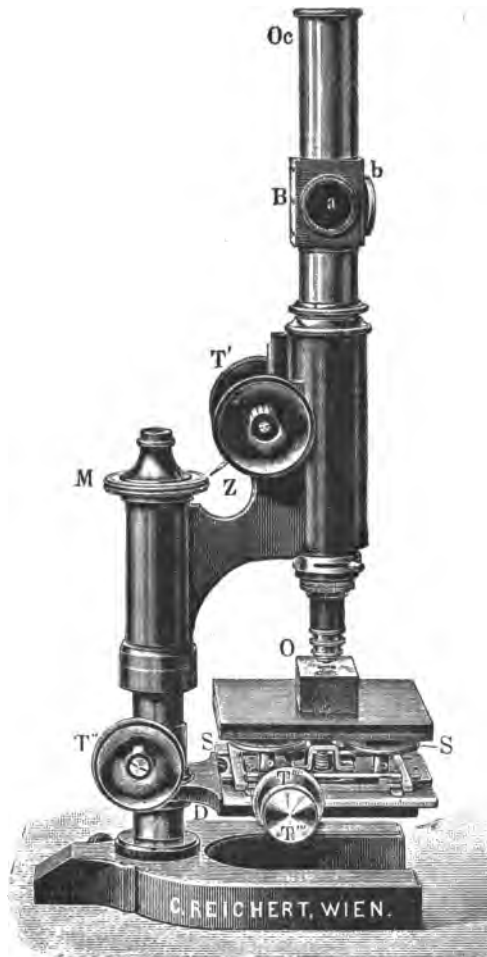
The object to be examined should have two parallel surfaces, so that it may be placed on the stage of the microscope in a perfectly horizontal position. With a view of compensating for small deficiencies in the parallelism of the two sur-

faces, the stage is provided with the screws SS, by which means it may be tilted, and the upper surface of the object made to lay in a truly horizontal plane, which of course is necessary in order to place the entire field in the focus of the instrument. The stage is a mechanical one, the milled heads T''' and T'''' imparting to it a forward and backward movement and a lateral movement, respectively.

After the source of light has been placed in the most desirable position for the examination of a certain specimen, if a sample of different thickness be placed on the stage, the microscope must be lowered or raised, with the result that the light is no longer in the proper position and must again be adjusted. To avoid this troublesome manipulation, the stage of the microscope is made adjustable in height, by turning the milled head T''. When the object is too thick to be placed on the stage, the latter may be turned to one side and the preparation laid on the foot of the microscope. For still larger pieces of metals, the stage may be removed altogether, the body of the instrument turned around 180°, and the metal placed on the table by the side of the stand.

Prof. Retjö's method for the preparation of the sample is as follows :

The piece of metal to be examined has two of its sides planed off and made parallel. The upper surface is polished until it is free from scratches. It is then washed with absolute alcohol, and wiped with a soft clean cloth in order to remove all fatty substances. The polished surface is next surrounded with a layer of wax so as to form a rim projecting a little above the surface. Being placed horizontally, pure concentrated hydrochloric acid is poured over it to a depth of about three millimeters, and allowed to act for five minutes. It is then poured off, and the surface covered with concentrated ammonia. The wax is removed and the surface wiped dry with a soft cloth. A little oil is next poured over it and allowed to remain for fifteen minutes. It is then dried again and rubbed on a piece of chamois leather until it assumes a shiny appearance.

When large pieces of metals are to be examined, small portions must be polished by hand and etched as described above.

Outfit for the Photomicrography of Metals. — Messrs.
QUEEN & Co. of Philadelphia have devised and placed on
the market a photomicrography outfit especially constructed
for recording the microstructure of metals. The arrange-
ment ·is plainly seen in the accompanying illustration, and
demands little explanation. It is simple, compact, and sub-
stantial in construction, and is especially well adapted, it
would seem, for quick work.

The camera may be tilted to one side for ocular examina-
tion of the object, selection of the spot to be photographed,
adjustment of light, etc., and then placed in a vertical posi-
tion and connected with the tube of the microscope. The
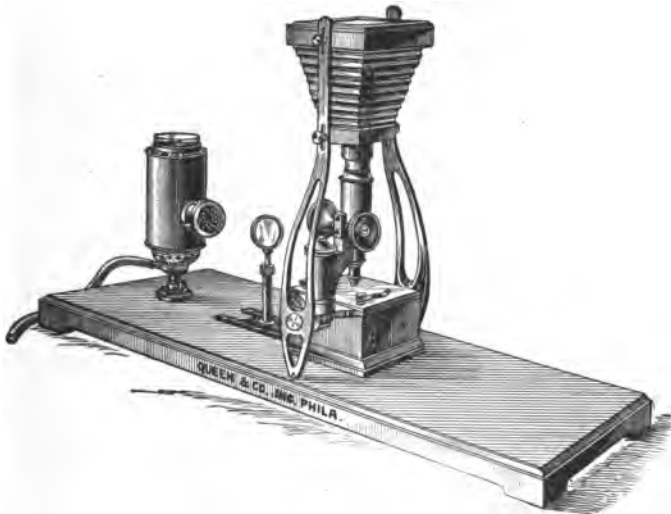
source of light is a Welsbach gas-burner, completely sur-
rounded by a metallic cylinder leaving only the necessary
aperture for the illumination of the object. ·

The emergent pencil of light may be controlled by an
iris diaphragm fastened to the burner. The light is received
by a condensing lens adjustable in height, and then by a
vertical illuminator screwed between the body of the micro-
scope and the objective. The Zeiss model of vertical illumi-
nator, consisting of a total reflecting prism covering half of
the aperture, is furnished with the instrument. Any other
form of illuminator, however, or the so-called " illuminating
objectives " may be used, if preferred.

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By ALBERT LADD COLBY, South Bethlehem, Pa.

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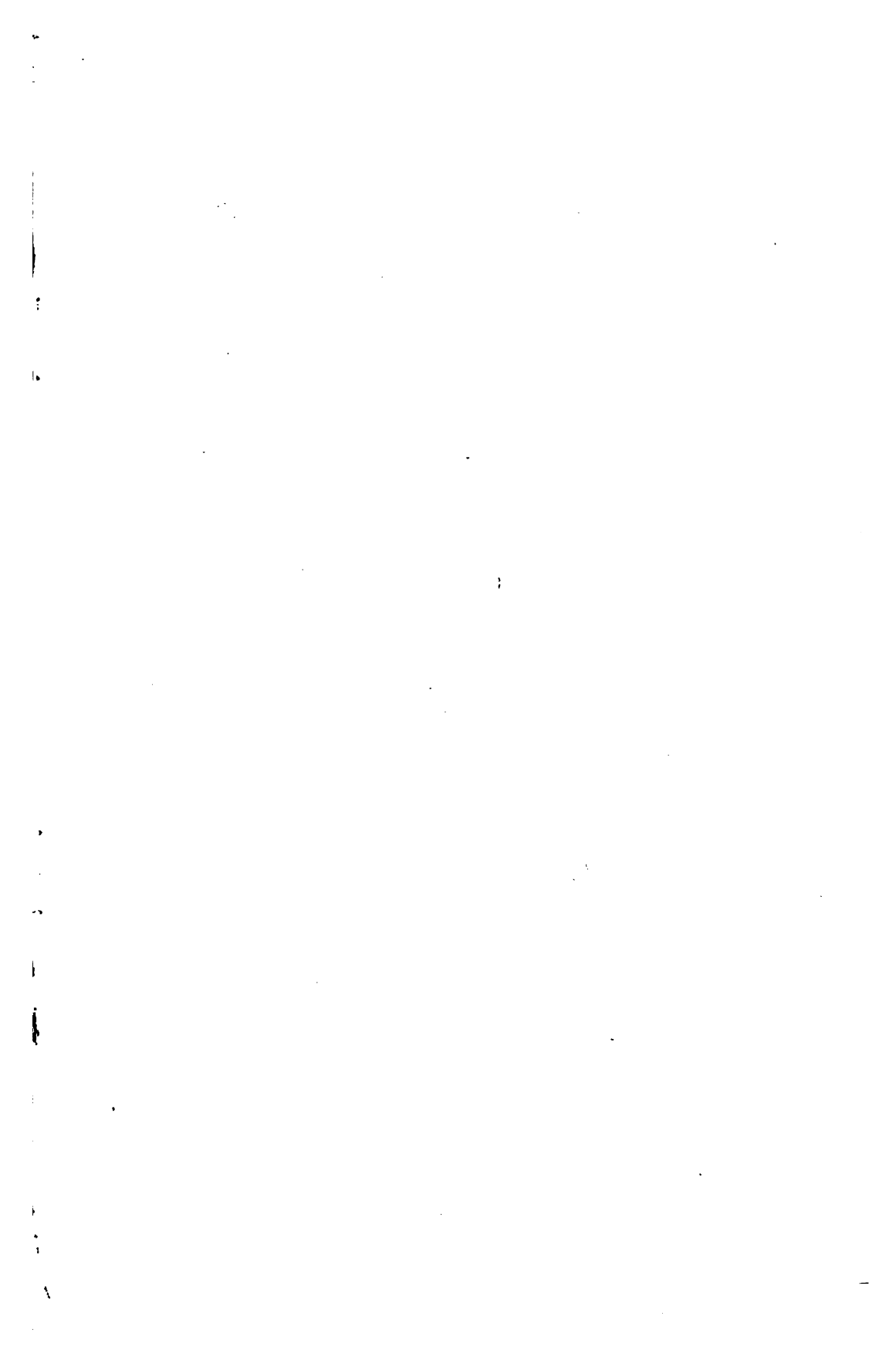
17. WERTH, J. — (See Osmond, Nos. 16 and 19.)

FIG. 13. Copper 80 per cent — Tin 20 per cent.
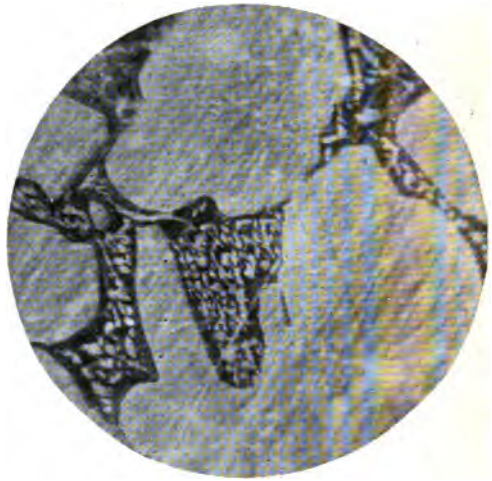Magnified 30 diameters.

FIG. 14. Copper 80 per cent — Tin 20 per cent.
Magnified 500 diameters.

FIG. 15. Copper 17 per cent — Tin 83 per cent.
Magnified 60 diameters.

FIG. 16. Industrial Bronze, showing crystals
of SnCu$_8$.

PHOTOMICROGRAPHS OF BRONZES, after CHARPY.

[See page 192 et seq.]

MICRO-CHEMICAL EXAMINATION OF LEAD-ANTIMONY ALLOYS.*

By JOHN E. STEAD, F.I.C.

IT would not appear, after reading all the available litera-
ture on the microstructure of alloys, that the compounds
of lead and antimony have been studied; I therefore prepared
a series of lead-antimony alloys, and the following description
of my work will, I hope, be of interest to the members of this
institution.

As the object was to ascertain the microstructure of alloys
which are commercially produced, virgin lead and best "star"
antimony, such as are regularly used in commerce, were em-
ployed in this research. Fifteen mixtures were made, in

In the introduction to his paper Mr. Stead reviews the work of
Charpy, Guillemin, Roberts-Austen, Arnold, Behrens, Osmond, and others.
The results of these investigators have, to a great extent, been either
published in full or reviewed in *The Metallographist*. The reader should
compare the results obtained by Mr. Stead with lead-antimony alloys,
with those of Mr. Charpy described page 95 et seq. (*The Metallographist*
for April, 1898).

Mr. Stead informs me that the first installment of his paper was
written before he had received Mr. Charpy's memoir. — ED.

which the proportion of lead and antimony varied between 1 per cent of antimony and 99 per cent of lead, and 95 per cent of antimony and 5 per cent of lead. The carefully weighed metals were introduced into plumbago crucibles containing fluid cyanide of potassium, which were then placed in a Fletcher's gas crucible-furnace. The lead in each case was first added, and when it was fluid and red-hot, the antimony was dropped in, and as it immediately sunk below the surface of the molten cyanide, practically no volatilization of antimony took place. The crucible with the contents was then vigorously shaken, to effect thorough admixture, and was allowed to slowly cool in the crucible in the open air. When cold, the cyanide was washed away by a running stream of water, and the solid metal or alloy was then removed by striking the mouth of the crucible upon an iron slab. Of course, the same crucibles were used over and over again, as it was not necessary to use a new one for each trial. The pieces of alloy weighed about 100 grammes, and measured about 1½ inch at the top, and were about 1 inch deep. Each sample was sawn vertically through the centre, and a complete section was then taken by cutting out a piece about $\frac{3}{16}$ inch in thickness.

Grinding and Polishing the Specimens. — After many trials it was found that the best way to obtain a perfectly flat face was to hold the section between the first finger and thumb, and to draw it downwards over the face of a smooth-cut file held vertically by the left hand, the tang resting upon a hard board or support. Having obtained a smooth surface, the next operation was to grind it upon a flat surface of Turkey-stone, such as joiners use for sharpening their tools; but instead of using oil, the stone was kept continually wet by the application of clear water. In a very few minutes of rubbing backwards and forwards, the file-marks were obliterated.

The following stage consisted in rubbing the specimen, with the application of practically no pressure, over a sheet of French emery-paper No. 0000.

It is important that no pressure, or at least practically no pressure, should be applied; otherwise the softer parts of the metal will be forcibly dragged or torn, and will overlap the harder parts of the structure.

The final stage consisted in rubbing the specimen over smooth cloth, free from ribs, upon which had been previously placed a small quantity of diamantine powder, a most valuable preparation, made in Switzerland, for the purpose of polishing steel, and which can be obtained from almost any jeweller. It is important that this block should be kept continually moist, otherwise the softer metal will be torn by the friction, and the specimen spoiled. It is also important that the pressure applied to the metal should be excessively light. The surface should be examined from time to time, and the polishing stopped as soon as the fine scratches, left by the emery, are obliterated. If the polishing is carried beyond this point, the softer constituents will be carried away, and the crystals or grains harder in character will stand in great relief, and be more or less rounded, and their true shapes rendered difficult to determine.

Etching the Polished Specimens. — After leaving the polishing-blocks, each specimen was thoroughly washed in water, and was at once, without drying, placed in a solution consisting of 99.5 c.c. of water, and ½ c.c. of nitric acid of 1.42 sp. gr. In about one minute the structure was usually sufficiently developed for a preliminary examination. It was then removed from the acid, thoroughly washed with water, and afterwards soaked in rectified spirit, after which it was removed, the excess of alcohol shaken off by swinging the specimen backward and forward, and was finally placed on a hot plate to dry, when it was ready for microscopic examination.

Description of Microstructures. — In the specimens containing between 1 and 13 per cent of antimony, the structure appeared to be almost amorphous, and it was difficult to determine the character of the crystals; but in the alloy containing 15 per cent of antimony there was found to be a distinct layer, clearly visible without magnification, of harder metal at the upper surface, that is to say, on that part of the metal which was uppermost when it solidified. In proportion as the antimony was increased this hard and silvery white layer increased in thickness, until when 50 per cent antimony was present, the whole mass appeared to be bright. On examining these white layers with an objective magnifying 50 diameters, it was noticed that they were not by any

means homogeneous, but consisted of more or less well-formed crystals apparently of cubical form, embedded in a substance exceedingly dark in color.

Having now crystallized out a definite structure, the next question was whether or not the alloy had separated into two fluid layers, one lighter than the other, previous to solidification, or whether the crystals had formed throughout the alloy, and afterwards floated up to the surface in a manner analogous but the reverse of that which occurs in crystallizing salt.

Messrs. C. R. Alder Wright and C. Thompson communicated a most important paper to the Royal Society, in 1889, on certain ternary alloys, in which the metals lead, tin and zinc in varying proportions were melted together, and the resulting mixtures, after slow cooling, were examined. It was found that if the tin is less than $\frac{3}{8}$ of the whole mass, the alloy divides itself into two different ternary alloys, lead preponderating in the heavier one; and they point out that this phenomenon is entirely distinct from the segregation of alloys during solidification, in consequence of the formation of other differently fusible alloys, and they also point out that the alloys separate as fluids, and then crystallize afterwards. In order to compare the microstructure of such alloys with that I had obtained, a mixture of tin, lead and zinc was prepared in the manner described by those gentlemen. A section of the mass was then made, and was examined under the microscope. The appearance clearly showed that the alloys had separated when in a liquid condition, for there was a clearly defined line between the upper and lower alloy, which was perfectly horizontal, the alloy above having an entirely different structure from that below the line of demarcation. In the lead-antimony alloys no such clearly cut line was present; in fact, as a rule, the upper layer was not horizontal, but curved downward on each side, and the matrix which constituted the lower part of the alloy could be traced continuously between the crystals to the very top of the mass. It was also noticed that several of the white bright crystals were present at the very bottom of the alloy, and it appeared that these had attached themselves to the bottom of the crucible, and were not, therefore, free to float through the mass.

Although such consideration would lead to the assumption that the crystals formed in the matrix at a temperature considerably above its melting-point, and then, in virtue of its less gravity, floated to the top, it was considered unsafe to form any conclusions without more practical demonstration. In order to settle the question beyond doubt, a considerable amount of an alloy containing 30 per cent of antimony and 70 per cent of lead, was melted and afterward poured into a mould which had been previously heated, and which was provided with rigid shelves, attached to one side of the mould only, and which projected half-way across, and which were fixed at an angle of about 30 degrees in an upward direction.

Fig. 1 will make the matter clear. It may be assumed
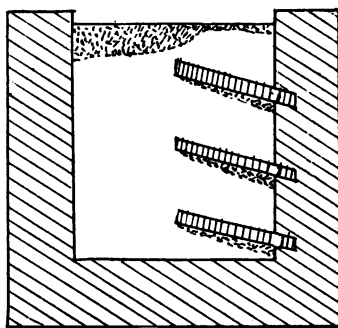
FIG. 1.

that if the lighter mass was in a fluid condition before it reached the surface, the shelves would not impede its progress. A liquid ascending would of course flow readily up the inclined planes and escape to the surface, whereas if it crystallized in the body of the mass, in ascending to the under sides of the shelves the friction would be too great to allow the crystals to travel upwards, and in making a section of the cold alloy, from top to bottom, one should then find layers of crystals under each shelf.

After pouring the alloy into the mould, it was allowed to cool very slowly, and when cold it was sawn from top to bottom, cutting it at right angle through the shelves. The whole mass was then polished and etched, and it was found,

as was naturally predicted, that the crystals on one half of the mould, where the shelves existed, were equally divided between the under sides of the three shelves and the surface. The above diagram is a graphic representation of the results obtained.

The next point of interest to determine was the composition of the hard white crystals. For this purpose a considerable quantity of the 30 per cent antimony alloy was melted, and cooled somewhat rapidly in a shallow iron mould, the object being to obtain the crystals unattached one to the other and suspended in the eutectic compound. This bar, measuring 6 inches by 2 inches by $\frac{1}{4}$ inch, was then filed bright, and was immersed in a 10 per cent nitric-acid solution in water, and it was allowed to remain there several days in the cold. On removing the bar from the acid, it was found to be coated with a soft, slimy material, in which the granular crystals were retained in position. By brushing off this deposit and washing with water, the dark-colored slime was removed, and the apparently pure white crystals separated as a heavy granular deposit. In order to thoroughly eliminate all adherent matter, these crystals were boiled with dilute nitric acid, but previous to doing this they were thoroughly well rubbed with the finger and thumb to separate adhering crystals, which might possibly enclose a portion of the eutectic alloy. After digestion with acid, they were thoroughly well washed in running water, and were afterwards dried. On examination under the microscope it was found that they consisted of more or less perfectly formed crystals of cubical form, and it was also observed that the angles had been but slightly acted upon by the acid, and as their surfaces were bright and continuous, we may be justified in assuming that the acid had not acted in any way upon the interior of their mass. The specific gravity of these crystals proved to be 6.5, which approximates to that of pure antimony, which is 6.7. An analysis showed them to contain 99.8 per cent of antimony and 0.2 per cent of lead ; in other words, they consisted of practically pure antimony. On examining the alloys containing more than 50 per cent of antimony, the crystals increased in volume until, when 95 per cent antimony was reached, practically the whole field under

the microscope appeared to consist of antimony, but even in this alloy a small quantity of the eutectic compound was most distinctly visible, surrounding more or less completely the square masses of antimony. As it was impossible to separate the crystals from the alloys containing a very large proportion of antimony, I am not in a position to state from actual trial that they do not contain some lead. The relatively small areas of the dark eutectic compound would lead us to believe that the white crystals in the 80 per cent and the 90 per cent alloys were not pure antimony.

The next question to determine was the character and composition of the eutectic or most fusible compound.

This was done by two different methods: first, by synthesis; and second, by analysis. It had been observed that there were hard crystals in the 15 per cent alloy, but none in that containing 10 per cent antimony. Several mixtures were made, containing between 15 per cent and 12 per cent antimony, and, after melting under cyanide and allowing them to cool slowly, they were cut up and examined. As the antimony was reduced, the hard upper layer decreased, until on arriving at a mixture containing 12.5 per cent antimony and 87.5 per cent lead, no separation of crystals could be detected, although they were clearly present in the alloy containing 13 per cent of antimony. If we take the atomic weights of lead and antimony to be 207 and 120 respectively, we find that a chemical compound having the formula Pb_4Sb would contain 12.66 per cent antimony and 87.34 per cent lead. On now melting the metals together in that proportion and allowing to cool slowly, we obtained an apparently homogeneous mass, free from separated crystals.

There was no difficulty in obtaining this material in a perfectly pure state, as it was only necessary to cut off the upper portion containing the free antimony of any of the alloys containing above 13 per cent of antimony, and to use the lower portion for analysis. Two carefully conducted determinations gave 12.8 per cent and 12.7 per cent of antimony and 87.2 per cent of lead, and this corresponds nearly with the formula Pb_4Sb. Although it was an easy matter to obtain the eutectic alloy from the alloys containing under 50 per cent, it was impossible to separate this material from

those containing 50 per cent and over of antimony. Recourse was therefore made to another method of research, namely, the determination of the freezing or critical points in cooling the liquid alloys. Each alloy was therefore carefully melted in a small charcoal crucible to a point considerably above the fusing-point, and by means of the Le Chatelier pyrometer a careful determination of the critical points was obtained. In applying the couple to the molten mass, the two twisted wires were first of all covered very carefully with moist asbestos-paper, in which condition it could be most readily moulded, so as to completely protect them from actual contact with the fluid metal. Previous to the introduction of the couple into the metal, the asbestos enclosing the couple was heated to bright redness in a bunsen flame, by which means the asbestos assumed a fair amount of rigidity. The actual thickness of this coating did not much exceed $\frac{1}{100}$ of an inch, and was so strong as to last for more than 20 determinations of tempera-ture without breaking. The pyrometer having been pre-viously most carefully calibrated according to the method given by Professor Roberts-Austen and others, and the alloys having been melted, it was only necessary to lower the asbestos-couple into the molten mass, and to pack loose fibrous asbestos all around it, over the surface of the liquid in the crucible, and then to carefully observe the points at which the speck of light became stationary or moved very slowly. The eutectic alloy had only one freezing-point — at about 247° C. The melting-point of lead being 325°, and that of antimony 630°, the mean of the two metals is 388°. It will be seen that the eutectic alloy had a solidifying-point of 388° — 247° = 141° below that of the mean of the two metals in the mixture, and 78° below that of lead. The alloy con-taining 95 per cent of antimony had a first critical point of about 615° C., and another of very short duration at 247° C., and all of the alloys had this one common point of 247° C., showing most clearly that the eutectic alloy in 95 per cent alloy was of the same composition as that containing about 13 per cent.

The specific gravity of the eutectic or lighter alloy was 10.48. Theoretically, the mean of the lead and antimony should have given a specific gravity of 10.77.

It is not surprising that the antimony crystals floated up to the top of the mass, considering that they were so much lighter than the eutectic alloy; in fact, the latter was more than 1½ times as heavy as the antimony.

Attempts were made to determine the crystalline structure of this eutectic alloy, but, as before stated, I failed to determine it by the usual methods of polishing and etching.* When, however, a sufficient quantity of the material was allowed to cool or solidify very slowly, the surface of the bright alloy presented a frosted appearance, and on examining this under high power, crystals of a hexagonal form were clearly detected.

When the proportion of lead is increased above 87 per cent, the pyrometrical results indicate two melting-points; the higher, or first freezing-point increasing with the increase of lead, until, when the whole of the antimony is eliminated, the melting-point is that of lead, or 325° C. Until that point is reached, however, there is a clear retardation at 247° C., showing that in this case the same eutectic alloy remains, as is the case in the alloys containing less than 87 per cent of lead.

In one case lead is dissolved in excess of the eutectic alloy, and in the other case antimony is in excess in the same mother-liquor.

That antimony and lead should combine in atomic proportions in the eutectic alloy is not contrary to the conclusions of Dr. Guthrie, who has thoroughly investigated eutectic compounds, his results having been communicated to the Royal Society in 1884 (*Philosophical Magazine*, Vol. 17, 1884, page 462), for that gentleman, although pointing out that such eutectic metals do not as a rule exist in atomic proportions, makes the following statement:

"When we are dealing with metals, which, like antimony and arsenic, on the one hand, are themselves homogeneous, or with such strongly chemico-positive metals as sodium, on the other, we may and do get alloys of atomic composition, metallo-metallic salts." It would not appear that Dr. Guthrie

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* Mr. Charpy states that a weak attack with nitric acid reveals the composite structure of this eutectic alloy; see page 95. Mr. Stead also succeeded in resolving it, as will be seen farther on. — ED.

had studied antimony and lead compounds; in fact, all his communicated results dealt with the compounds with bismuth, zinc, tin, lead and cadmium, and with mixed salts; and he clearly demonstrated that the eutectic, or most fusible constituent of each alloy, did not have the metals in any simple atomic proportion. To use his own words, "The constitution of eutectic alloys is not in the ratio of any simple multiple of their chemical equivalents, but their composition is not on that account less fixed, nor are their properties less definite."

The same gentleman showed that there was a close relation between the eutectic compound metals and the cryohydrates of common salts in water, and states, "For as a salt may unite with water, as when anhydrous chloride of calcium does so, to fix the water as crystalline water, and also may unite with water as a cryohydrate, so two metals may unite in one proportion, while they form a definite eutectic alloy in another."*

Henri Gautier (*Comptes Rendus*, 1896, pages 109–113) makes the following interesting statement with reference to the fusibility of metallic alloys: "Fused alloys, on solidification, behave in a similar manner to fused mixtures of salts, and hence may be divided into three classes corresponding with the three classes of saline mixtures recognized by Le Chatelier.

"(1) The metals do not combine in any fixed proportions, and the two constituents crystallize quite distinctly; for example, alloys of tin with zinc, bismuth, or lead.

"(2) A definite compound of the two metals crystallizes out, but these crystals are scattered in a crystalline matrix of the metal which is in excess; for example, copper with tin or antimony.

"(3) Alloys corresponding with isomorphous mixtures of salts; for example, gold and silver.

"The fusibility-curve of an alloy at once indicates to which of these three classes the alloy belongs."

In concluding this section it is necessary to point out that various chemical and metallurgical text-books contain

* In the next article of the present number of *The Metallographist* the reader will find further evidences of the analogy between the cryohydrates of saline solutions and the eutectic mixtures of metallic alloys. — ED.

most erroneous statements with regard to the melting-point and equivalent of antimony.

The chemical equivalent is given in many books as 122 instead of 120, and the melting-point as 430° C. instead of 630° C.; in fact, my own observation proves that antimony and aluminium have practically the same melting-point, namely, about 630°, and Henri Gautier gives the melting-point at 632°.

[The following further remarks concerning alloys of lead and antimony constitute a portion of the second installment of Mr. Stead's paper, and were written after the author had read Mr. Charpy's memoir on metallic alloys, concluded in the present number of *The Metallographist.* — ED.]

So far as our microscopic work is concerned, our results agree closely, but Mr. Charpy has more fully studied the structures of lead-antimony alloys containing less than 13 per cent antimony than I had done at that time; and I, on the other hand, had supplemented the microscopic investigation with a chemical research, with the object of determining the composition of the separated crystals.

Mr. Charpy had great difficulty in polishing the alloys containing less than 13 per cent of antimony, and it will be remembered that I experienced the same thing, and resorted to the examination of the surface of the solidified eutectic of the lead-antimony alloys instead of the polished and etched surfaces. On further attempts to develop the structure by etching this eutectic, and of the alloys containing less than 13 per cent antimony, I have recently been more successful. After long-continued action of dilute nitric acid on the eutectic, it was observed that a thick adherent layer, almost black, covered the polished surface. A portion of this was removed and was, after well washing with water, tested for lead, and as it was found to be absent we may conclude it was pure antimony.

After rubbing away the dark layer by gentle friction under running water, the metal below presented a most characteristic microscopic appearance. At fairly equable distances apart, what appeared to be laminæ radiated from nuclei, and continued in right lines until met by similar radiations from other nuclei. The accompanying photograph

(Fig. 2) clearly illustrates this. The appearance is similar
to that of nodules of pyrites with radial structure or spher-
ulites in obsidian.

On examining the dark crust after gently crushing so as
to separate the individual particles of antimony, it was found
that it consisted of very fine, thin plates, as the microscopic
appearance of the etched specimen would lead us to suppose;
and these, on further pressing, appeared to split up into
excessively fine rod-like bodies, which, but for their absolute
opacity, might be mistaken for certain forms of bacteria.

Every metal I have examined, and many alloys, appear

FIG. 2.   Eutectic Alloy of Lead and Antimony.

to be built up of laminæ, and such laminæ are themselves
built up of crystals of definite form. The lead eutectic is no
exception to the rule, and it appears certain that it is con-
stituted of alternate laminæ of lead and antimony, as Mr.
Charpy suggests. The composition of this eutectic is, as
before pointed out, that of the atomic proportion of Pb_4Sb;
but there can be no doubt, judging from the fact just referred
to, in the solid state they are not in chemical union.

Whether this eutectic is analogous to a cryohydrate, or
at its melting-point when fluid is a chemical compound which
afterwards, simultaneously with solidification, splits up into

its elements, remains to be determined. The fact that it has a distinct tendency to crystallize in hexagonal forms, whereas both constituents separately at the solidification-point give skeleton octahedra, strengthens the latter hypothesis. Fluid gray iron simultaneously solidifies and splits up into iron and graphite, and may be an instance analogous to what takes place in the eutectic.

It has already been shown by the critical points on cooling, that in the alloy containing less than 12.7 per cent antimony, the lead crystallizes in the eutectic. Mr. Charpy has demonstrated that this is so by the microscope, and I have recently obtained an excellent illustration of this from an alloy containing 10 per cent antimony and 90 per cent lead, in which the dendritic crystals of lead are clearly developed in a eutectic matrix, thus confirming Charpy's results.

The structures or surface-markings of small ingots of alloys after solidification, without any preparation, frequently are similar and sometimes identical with those obtained by the more laborious methods of grinding and polishing. This is the case with some of the alloys of tin and copper, tin and arsenic, tin and lead, lead and antimony. The surface of an ingot or small cake of a lead-antimony alloy containing 10 per cent of antimony has upon its skeleton octahedron lead crystals and the spherulitic structures of the eutectic side by side. If the antimony present does not exceed 6 per cent, the eutectic sinks below the mass of lead crystals, which solidify first, leaving the latter in strong relief; it is therefore impossible, in such cases, to obtain on the surface indications of the structure of the eutectic.

As the eutectic on digestion in nitric acid has all of its lead dissolved away, leaving the antimony intact, and in a mass of the same bulk as the original alloy, and also fairly coherent, it was believed that when there were free fir-tree crystals of lead in the solid eutectic, they would be dissolved away by acid, leaving cavities where they originally existed, and that on breaking the coherent and porous mass after drying it, these cavities would be visible on the fractured surfaces. On making the experiment this was proved to be the case ; the empty areas where at one time lead had crystallized were clearly visible.

The solid eutectic of lead and tin consists of similar masses of spherulites. They can be easily seen on the surface of an ingot carefully cooled, and if, when the alloy is partially solidified and is poured out suddenly upon an iron plate, they are readily detected, for they stand out as little nobs above the surface of what was, at the time of forming, liquid metals. The spherulites being solid, the still liquid metal falls away, leaving the nobs referred to.

When alloys of antimony and lead with between 15 per cent and 40 per cent are caused to solidify very slowly, the crystals of antimony do not separate in the mass and then float to the surface, but begin to form at the surface and slowly grow downwards, and the crystals branch out, and are more or less perfectly joined together, and the ends terminate in the eutectic below.

MICROSCOPIC STUDY OF METALLIC ALLOYS.

By G. CHARPY.

IV. Alloys with Abnormal Curves of Fusibility.

Alloys of Copper and Tin. — The different properties of alloys of copper and tin have been studied more than those of other alloys. From the comparison of the results of the various researches one is led to admit the existence of a definite compound answering to the formula $SnCu_8$, for which compositions discontinuities are found in the variations of a great many properties, notably in the electric conductibility, according to Mathiessen; in the electro-motive force of dissolution, according to Laurie; in the specific gravity, according to Riche; and in the coefficient of dilatation, according to Grace-Calvert.

Mr. H. Le Chatelier, moreover, has isolated some crystals corresponding to the formula $SnCu_8$ in treating with hydrochloric acid, alloys richer in tin, and Mr. Laurie states that if in a copper-chloride battery the zinc be replaced by a copper-tin alloy, rich in tin, pure tin is rapidly dissolved, and the compound $SnCu_8$ is left, almost pure, its composition not

undergoing any further change if it be protected against the atmosphere. The curve of fusibility, determined by Mr. Le Chatelier, is composed of three branches forming by their intersections two angular points corresponding to alloys with 3 and 72 per cent of copper, respectively; the intermediate branch does not exhibit any maximum, in which it differs from other alloys such as copper-antimony alloys.

The solidification of alloys of copper and tin has been studied recently by Roberts-Austen and Stansfield, who have determined not only the temperatures corresponding to the beginning of solidification, but the whole cooling-curve of the alloy; they have detected in this way successive evolutions of heat indicating that solidification occurs partially at different temperatures.

The alloy containing 75 per cent of copper, for instance, exhibits, besides the evolution corresponding to the beginning of solidification, which consists probably in the separation of crystallites of pure copper, a second liberation of heat at about 770° C., corresponding to the solidification of the first eutectic alloy. A third evolution of heat is sometimes detected between 500° and 600°, whose meaning has not yet been ascertained. In alloys rich in tin an evolution of heat occurs at about 227°, and corresponds to the solidification of the second eutectic alloy.

The microscopic structure of bronzes has been studied by Mr. H. Behrens, who divides them in two principal groups: bronzes rich in copper, containing from 1 to 25 per cent of tin, and bronzes rich in tin, containing over 25 per cent of tin. With the exception of the metal for mirrors (25 to 35 per cent of tin), which appears homogeneous, Mr. Behrens says that in all bronzes, a portion, rich in copper or rich in tin, may be detected, forming the fundamental mass, the former in alloys rich in copper, the latter in those rich in tin.

Both portions may readily be seen in alloys containing from 0 to 25 per cent of tin, the former presenting a redish-yellow color, while the latter appears nearly white. Polishing alone suffices to separate the two substances in alloys containing from 18 to 25 per cent of tin. In metals richer in copper it is preferable to etch the preparation slightly with hydrochloric acid, and then to polish it again very gently; white

portions with sharp outlines may then be distinctly seen, in amounts varying with the percentage of tin in the alloy. This white substance surrounds dendrites having an intense yellow color. High power shows this white substance to be made up of two constituents, one white and the other çolored; it probably corresponds, therefore, to the first eutectic alloy, containing 27 per cent of copper. Bronzes rich in copper may be compared, therefore, to the alloys of copper and antimony containing from 0 to 31 per cent of copper; they present, however, some peculiarities to which we shall presently return.

Fig. 13 (Frontispiece) shows the structure of a bronze containing 20 per cent of tin, magnified 30 diameters. The composite structure of the eutectic alloy does not appear under such low magnification, but it is readily seen in Fig. 14 (Frontispiece), which exhibits the same alloy magnified 500 diameters. [This figure was reproduced from a negative print, so that here the background appears white instead of dark. The appearance of the constituents of the eutectic alloy is likewise reverse. — ED.]

The study of alloys rich in tin has led us to classify them into several groups similar to those of antimony-copper alloys.

Alloys containing from 0 to 3 per cent of copper are very soft, very difficult to polish, yielding unsatisfactory preparations; long dendrites may be detected, however, probably of tin, surrounded by a matrix in which some very thin, hard, crystalline trails (*traînées*) are discernible.

In the alloy containing 10 per cent of copper very hard crystals are found, embedded in a matrix very delicately laminated. These hard crystals have a tendency to form six pointed stars which are very sharply outlined when the cooling is sufficiently slow; they increase in quantity with the percentage of copper, until they constitute the whole mass of the alloy.

Fig. 15 (Frontispiece) shows under a magnification of 60 diameters the structure of an alloy containing 17 per cent of copper, and cast in a metallic mould. The specimen was polished and etched with hydrochloric acid. The white needles represent the hard substance unaffected by the acid, probably the compound $SnCu_3$.

Fig. 16 (Frontispiece) reveals some crystals of $SnCu_3$, made apparent by polishing, in an industrial alloy prepared in large quantity.   The solidification having taken place more slowly, the crystals are more fully developed and form star-like groups.

Alloys containing from 55 to 65 per cent of copper have a structure which is quite homogeneous and difficult to resolve.   As the composition of the alloy approaches that of the eutectic mixture (73 per cent Cu), however, some hard crystalline grains are detected, surrounded by a substance somewhat colored, and which is much more readily oxidized by heating than by electrolysis.

Fig. 3 of the plate facing page 87 (Frontispiece, Vol. I. No. 2), which refers to a copper-antimony alloy, gives also the exact appearance of a copper-tin alloy containing 70 per cent of copper.

The structure of alloys of copper and tin varies, therefore, like that of copper-antimony alloys.   The region, between the two eutectic mixtures, in which the alloy is quite homogeneous, is, however, sensibly wider.   It is interesting, in this connection, to recall the fact that the fusibility-curve does not exhibit, in this region, the maximum which corresponds to definite compounds.

Alloys containing less than 27 per cent of tin present another peculiarity.   In such alloys, and especially in those richer in copper, the proportion of eutectic alloy is, in many cases, decidedly too small to infer that the metal is made up of dendrites of copper surrounded by the eutectic mixture. Upon closer investigation it was found that the rate of cooling had a marked influence upon the proportion of the eutectic alloy present in the metal.   In quickly cooled alloys the eutectic mixture may even disappear almost completely, notwithstanding the presence of some 7 or 8 per cent of tin; while in slowly cooled alloys, containing only 2 or 3 per cent of tin, a certain amount of the eutectic alloy is readily discernible.   It might be supposed that it is due only to a variation in the size of the particles of the eutectic alloy, but by following with the microscope the progress of the oxidation, produced by ammonia, for instance, one is led to infer that dendrites of nearly pure copper are formed first, and are then

covered by a layer of an alloy of copper and tin, leaving a small amount only of a substance nearly identical in composition to the eutectic alloy.

If an alloy of this group, after having been etched with hydrochloric acid and again polished so as to reveal the white grains of the eutectic alloy, be treated with ammonia, the portions further away from those grains are first oxidized, the oxidation spreading rapidly over a certain area, and forming dark dendrites, surrounded by bands much lighter, and in

FIG. 17.   Alloy of Copper and Tin.
Cu 90 per cent — Sn 10 per cent.   Magnified 500 diameters.

the middle of which white grains are found which may be resolved in two components, by high power.

Fig. 17 shows the structure, magnified 500 diameters, of a bronze containing 10 per cent of tin and prepared in this way.   Particles of the eutectic alloy may be seen, sharply outlined, in the middle of areas almost as light, while the portions furthest away appear dark.   When a metal, which exhibits distinctly the presence of some eutectic alloy, is heated to a red heat and then suddenly cooled, a structure is produced very similar to that resulting from a sudden cooling from the molten condition.   These phenomena might

possibly be compared to those which produce the hardening of steel. Although giving rise to effects much less intense, they are, nevertheless, interesting. It is our intention to again take up this matter at some future time.

Alloys of Antimony and Tin. — The curve of fusibility of alloys of antimony and tin, determined by Mr. Roland-Gosselin, constitutes the only knowledge we have regarding the physical properties of these alloys. Their fusibility-curve is altogether different from those obtained in the case of all the other alloys which have been studied; it it composed of three branches with their concavity turned upwards, and giving by their intersection two angular points, whose position is the reverse of that which generally corresponds to eutectic alloys. The curve does not give *a priori* any indication concerning the reciprocal relations of tin and antimony.

The structure of these alloys, however, may be easily studied. Beautiful preparations are readily obtained by polishing followed by a light etching with diluted hydrochloric acid. In alloys containing 5 per cent of antimony, long needles may then be seen in a matrix containing some hard and extremely small grains. Such appearance seems to indicate that they are composed of crystalline particles of tin in a eutectic mixture.

With 10 per cent of antimony in the alloy, some white, hard crystals, cubic in shape, may be detected on the polished surface. They remain unaltered after a light etching with diluted hydrochloric acid, while the matrix is somewhat dug out. The structure of the matrix is identical to that of the alloy containing 5 per cent of antimony. The quantity of these white crystals increases proportionally with the percentage of antimony. They finally unite in long files of crystals, altogether similar to those formed by the antimony in alloys of antimony and silver, or of lead and antimony. When the alloy contains about 50 per cent of antimony, it appears to be made up entirely of these crystals.

Figs. 18 and 19 show the structure of alloys containing respectively 10 and 25 per cent of antimony.

Alloys containing from 45 to 55 per cent of antimony present the same appearance, the metal being then nearly homogeneous. It contains numerous crevices which are in-

tensified by etching. A prolonged etching reveals around the edges of these crevices a secondary crystallization free from intermediate substance. Such characteristics seem to indicate the existence of a definite compound containing about 50 per cent of antimony.

An alloy with 60 per cent of antimony exhibits after polishing some hard crystalline needles, intricately united, and which possess the same characteristics as those described in connection with alloys of bismuth and antimony. They are not isolated in the middle of a softer mass, but constitute
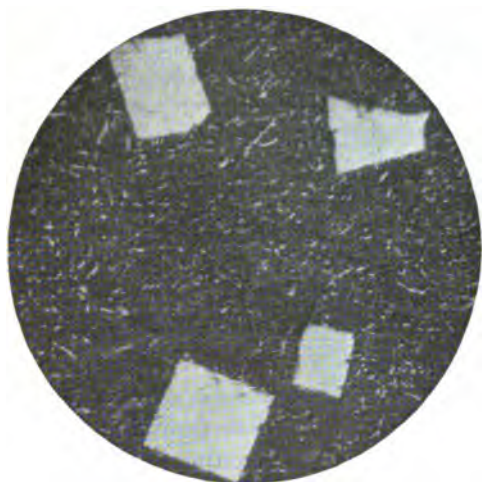
FIG. 18. Alloy of Tin and Antimony.
Sn 90 per cent — Sb 10 per cent.

FIG. 19. Alloy of Tin and Antimony.
Sn 75 per cent — Sb 25 per cent.

the edges of hillock-like formations. This peculiar structure, which seems to indicate that the alloy is an isomorphous mixture, is best seen under low magnification and by oblique light. It is difficult to etch the preparations properly; the best results are obtained through oxidation by electrolysis in a nitric-acid solution. It may then be seen that the lower portions are oxidized first, the oxidation spreading gradually over the whole surface. Fig. 20 shows the structure of an alloy containing 60 per cent of antimony and partially oxidized by electrolysis.

Alloys containing still more antimony present the same features; the shape of the hard crystals, however, varies, gradually assuming more and more the characteristic outlines of crystals of antimony.

The microscopic study of alloys of antimony and tin would, therefore, lead to admit the existence of a definite compound containing about 50 per cent of antimony, and which forms with that metal isomorphous mixtures.

Alloys of Antimony and Silver. — The curve of fusibility of antimony-silver alloys, determined by Mr. H. Gautier, is

FIG. 20.   Alloy of Tin and Antimony.
Sn 40 per cent — Sb 60 per cent.   Magnified 30 diameters.

composed of two branches which meet at a point corresponding to a eutectic alloy (50 per cent silver).   These two branches, however, are irregular in shape; they each have a point of inflection, one of them, very slight, corresponding to an alloy with 20 per cent of silver, the other, very marked, corresponding to an alloy containing about 80 per cent of silver.

Alloys rich in antimony are very hard and take readily a fine polish.   The polishing operation is sufficient to reveal the presence of hard crystals of antimony embedded in a

eutectic alloy, which increases in proportion with the per-
centage of silver. A nitric-acid etching colors the matrix
and yields beautiful specimens.

Fig. 21 exhibits the structure of an alloy containing
16 per cent of silver. The crystals of antimony are still, to
a great extent, arranged in rows. A few white dots may be
detected in the matrix; they suggest the composite structure
of the eutectic alloy. In Fig. 22, which reveals the structure
of an alloy containing 25 per cent of silver, the crystals of
antimony are isolated, some of them forming star-like groups,
but they retain the same general configuration.

These reproductions will suffice to illustrate how the
structure of the alloys corresponding to the first branch of
the fusibility-curve varies. The variation of their structure
is, in every way, similar to that of the structure of alloys
of antimony and lead, already described. The faint point of
inflection of this first branch does not seem to correspond to
any peculiarity of the microscopical appearance of the alloys.

With a greater percentage of silver than that of the
eutectic alloy, the metal has an entirely different appearance.
The alloys, which are then much softer, may still be well
polished, but the polishing is not sufficient to reveal the
structure. On etching with dilute nitric acid, the presence
of rounded crystallites is disclosed, embedded in a eutectic
alloy distinctly made up of plates alternately soft and very
hard, the latter having the appearance of antimony. The
silver may also be colored by sulphuretted hydrogen, or the
preparation may be acted upon by concentrated ammonia,
which covers the antimony with a thin film of dark-blue
oxide, while the silver is left unaltered.

Fig. 23 shows the structure, magnified 30 diameters, of
an alloy containing 66 per cent of silver. The light portions
correspond to the crystallites, the dark areas to the eutectic
alloy. The structure of the latter is not resolved by such
low magnification, but it has already been illustrated in
Fig. 2 of the plate facing page 87.

With further increase of silver the crystallites unite,
forming long dendrites, but at the same time appear the
characteristic features of isomorphous mixtures, already
described. It is not possible, whatever the method used, to

separate these dendrites very distinctly from the surrounding matrix.

FIG. 21.   Alloy of Silver and Antimony.
Ag 16 per cent — Sb 84 per cent.

FIG. 22.   Alloy of Silver and Antimony.
Ag 25 per cent — Sb 75 per cent.

FIG. 23.   Alloy of Silver and Antimony.
Ag 66 per cent — Sb 34 per cent.   Magnified 30 diameters.

These considerations would seem to indicate the existence of a definite compound, forming isomorphous mixtures, with silver.

Several series of planimetric measurements of various samples containing 66 per cent of silver gave nearly concordant results, and indicated that about two-thirds of the mass was made up of crystallites. They cannot be, therefore, pure silver, since the alloys experimented upon contain 66 per cent of silver, and the eutectic alloy 55 per cent.

From the chemical composition of the alloy and these planimetric measurements it would seem to follow that the crystallites contain about 28 per cent of antimony, which correspond to the formula $SbAg_3$.

Alloys of Copper and Zinc. — The microstructure of copper-zinc alloys has been studied by Mr. Behrens, who mentions the probable existence of the following definite compounds: $CuZn$ (51 per cent Zn), $CuZn_2$ (67.8 per cent Zn), and $CuZn_4$ (80.3 per cent Zn). He finds that brass containing 20 per cent of zinc, or less, has a structure similar to that of red copper, only the crystals are here embedded in an intermediate, yellow substance. With percentages of zinc varying from 20 to 40, the structure becomes more like that of bronze containing about 15 per cent of tin. The intermediate substance, however, is as hard as the crystals, and is the more intensely yellow the greater the proportion of zinc. With nearly 50 per cent of zinc "the rows of crystals," Mr. Behrens says, "become thinner and less numerous; the crystals and the matrix assume nearly the same color."

"Alloys containing nearly the same number of atoms of copper and zinc sometimes exhibit only slight signs of crystallization."

Alloys containing 50 per cent of zinc show, after an ammonia treatment, "a net-work of curved lines on a yellow background, uniformly colored. An alloy with 67 per cent of zinc assumes a uniform coppery appearance when treated with sulphuric acid; it appears quite homogeneous and contains some crevices; it corresponds to a critical point in the variation of the hardness of the alloys."

In alloys richer in zinc, Mr. Behrens again finds the structure made up of crystals and of a fundamental mass

which increases with the percentage of zinc. From the varia-
tion in the shape of the crystals, and from the difficulty of
resolving the structure of the alloy containing 80 per cent
of zinc, Mr. Behrens infers the existence of a definite com-
pound, $CuZn_4$.

Our results agree partially only with those of Mr. Beh-
rens. In alloys whose compositions approach that of $CuZn_2$,
we find, like him, a structure quite homogeneous, great hard-
ness and some crevices. These characteristics indicate the
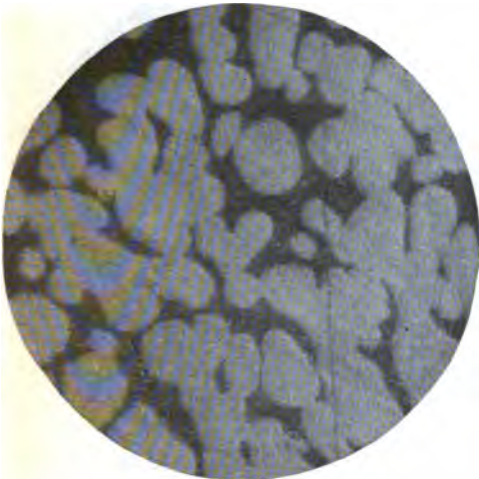
FIG. 24.   Alloy of Copper and Zinc.
Cu 10 per cent — Zn 90 per cent.

FIG. 25.   Alloy of Copper and Zinc.
Cu 25 per cent — Zn 75 per cent.
Magnified 100 diameters.

existence of a definite compound, which is confirmed, more-
over, by other phenomena.

Alloys containing over 67 per cent of zinc exhibit their
structure very distinctly when treated with caustic potash.
Their appearance leads to their classification in two groups :
in the first group, alloys containing from 0 to 20 per cent of
copper; in the second, alloys containing from 20 to 33 per cent
of that element.

Alloys of the first group, i.e., richer in zinc, are com-
posed of rounded crystallites, embedded in a metal which hot
caustic potash readily dissolves. Unlike eutectic alloys, this

metal is structureless, and no copper remains from its dis-
solution in caustic potash. It is probable, therefore, that it
is made up of nearly pure zinc. Fig. 24 shows the structure
of an alloy containing 90 per cent of zinc, and treated with
caustic potash.

    With 20 per cent of copper, the alloy appears quite
homogeneous. It is slowly attacked by caustic potash, and
assumes a uniform coppery appearance.   It has all the
characteristics of a definite compound, and corresponds to
the formula $CuZn_4$.

    With 25 per cent of copper, the alloy contains some white,
hard crystallites embedded in a matrix presenting exactly
the appearance of eutectic alloys (Fig. 25). Caustic potash
dissolves one of the constituents of this matrix, leaving a
light copper residue ; it is probably the compound $CuZn_4$.

    It would seem from the above considerations, that the
curve of fusibility is more complicated than the one indicated.
The small number of measurements taken in this region does
not permit our being affirmative upon this point.

    In alloys containing much copper, a structure is found
which recalls that of copper or of bronze, being made up of
long dendritic needles. We could not detect, however, any
intermediate substance, sharply defined. The crystals possess
the characteristics of isomorphous mixtures, oxidations tak-
ing place in a way similar to that observed in the case of
bronzes, although there is here no constituent corresponding
to the eutectic alloy. It seems probable, therefore, that these
metals are not made up by the juxtaposition of two different
alloys, but that they are composed of crystals whose composi-
tion possibly varies, but which make up the whole mass.
Such view is confirmed by the appearance of the structure
after annealing, which is then found to be composed in-
tegrally of a single kind of crystals. It should also be re-
called, in this connection, that Professor Roberts - Austen
found that alloys containing from 0 to 30 per cent of zinc have
only one point of solidification. In the case of alloys richer
in zinc, on the contrary, the same observer detected a second
freezing-point at a much lower temperature. The microscop-
ical examination of these alloys also reveals a very distinct
separation between the crystallites and the surrounding sub-

stance. This structure is readily made apparent through oxidation brought about by heating the preparation, or by treating it with ammonia, caustic potash or dilute acids. Fig. 26 shows the structure of an alloy containing 40 per cent of zinc and etched with ammonia. The substance surrounding the crystals is alone colored by such treatment. The structure of that substance is itself formed by the agglomeration of very small crystals, imparting to it a granular appear-

FIG. 26. Alloy of Copper and Zinc.
Cu 40 per cent — Zn 60 per cent.
Magnified 200 diameters.

FIG. 27. Alloy of Copper and Zinc.
Cu 50 per cent — Zn 50 per cent.
Magnified 200 diameters.

ance, but unlike the eutectic alloys it does not reveal the presence of two juxtaposited constituents.

In alloys containing as much as 60 per cent of zinc, two components may still be detected after polishing. The structure is made up of yellow-colored grains surrounded by a white net-work (Fig. 27).

The structure of copper-zinc alloys is therefore more complicated than that of most alloys. It seems very probable that the composition of the crystals varies continuously, within certain limits, with the composition of the metal. Besides this peculiarity five types of structure must be noted :

(1) From o to 33 per cent of zinc, dendrites constituting the whole mass and probably composed of isomorphous mixtures.

(2) From 33 to 45 per cent of zinc, rounded crystallites, embedded in a metal composed of small crystals which, however, cannot be resolved in two constituents.

(3) From 45 to 67 per cent of zinc, yellow crystalline grains containing many small white crystals and welded together by means of a white alloy.

(4) From 67 to 80 per cent of zinc, white crystallites, embedded in an alloy which like the eutectic mixtures is made up of two constituents.

(5) From 80 to 100 per cent of zinc, rounded crystallites, embedded in a metal which cannot be resolved in two components.

The points of transition correspond to the compositions indicated by the formula $CuZn_3$, $CuZn_4$, Cu_2Zn and possibly $CuZn$.

This complexity of constitution very likely corresponds to the great variety of properties of brasses of different compositions.

Alloys of Silver and Tin. — The curve of fusibility of alloys of silver and tin, determined by Mr. H. Gautier, is composed of two branches meeting at a point corresponding to the eutectic alloy, which contains about 5 per cent of silver. The branch which starts from the melting-point of silver exhibits two points of inflection corresponding to the alloys containing about 40 and 70 per cent of silver.

The hardness of these alloys varies very much and is considerable between 60 and 85 per cent of silver. Mr. H. Behrens, who has studied these alloys, observed two maxima in the hardness, one corresponding to 65 per cent, the other to 80 per cent of silver. Between these two alloys the hardness, according to our experiments, varies very little.

Mr. Behrens selected some alloys of silver and tin for the purpose of ascertaining the existence of definite compounds. He obtained, by fusion, crystals answering to the formulas Ag_6Sn, Ag_4Sn, Ag_3Sn, Ag_2Sn, $AgSn$, Ag_2Sn_3, $AgSn_2$. "The last three samples," Mr. Behrens says, "gave a certain amount of a softer mother-solution; the first four samples

appeared homogeneous. The existence of a series of combinations of silver and tin cannot be doubted.''

The fact that well-defined crystals are obtained through fusion, does not seem to us sufficient to characterize a definite compound, for the same phenomenon occurs in the case of isomorphous mixtures. The study of silver-tin alloys has led us to believe that they exhibit isomorphism-phenomena.

The alloy containing 10 per cent of silver reveals, after polishing, the presence of hard crystals surrounded by the eutectic alloy. The structure is more marked after etching
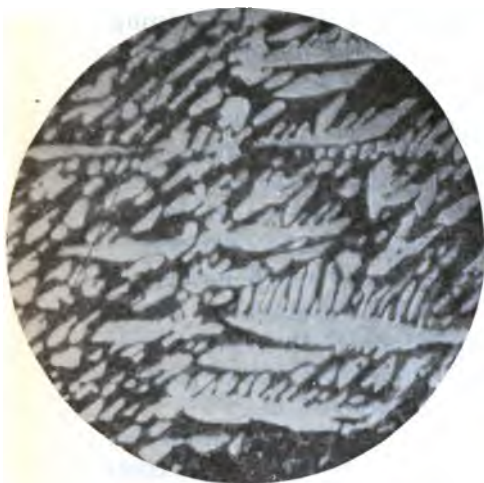
FIG. 28. Alloy of Silver and Tin.
Ag 33 per cent — Sn 67 per cent.
Magnified 30 diameters.
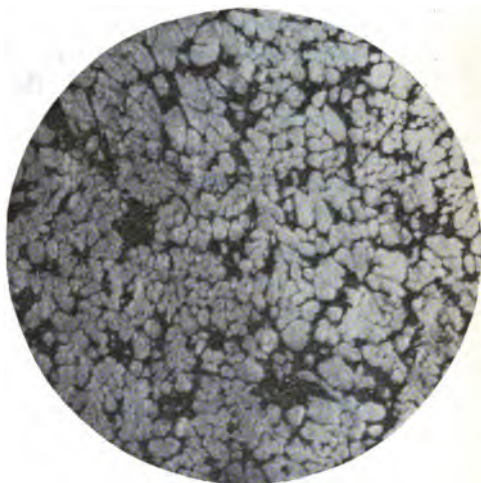
FIG. 29. Alloy of Silver and Tin.
Ag 45 per cent — Sn 55 per cent.

with hydrochloric acid ; some minute crystalline trails (*traînées*), unaffected by the etching, may then be detected in the eutectic alloy and appear to be made up of the same component as the isolated crystals. The number of crystals increases correspondingly with the proportion of silver in the alloy. With 30 per cent of silver, they are united, forming dendrites. With 50 per cent of silver the hard constituent occurs as rounded crystallites very close to each other.

Fig. 28 shows the structure of an alloy containing 33 per cent of silver. The crystals appear white, the eutectic alloy,

attacked by the acid, is dark. In Fig. 29, showing the structure of an alloy containing 45 per cent of silver, the crystals are much more numerous. With 60 per cent of silver, the eutectic alloy disappears almost entirely.

Alloys containing more silver are quite homogeneous. With 75 per cent of that element a dendritic structure appears, comparable, in every respect, to that of brasses rich in copper. Oxidation, brought about through electrolysis, outlines some dendrites without revealing any intermediate substance, and gradually encroaches upon the whole mass.

These results seem to point to the existence of a definite compound containing about 70 per cent of silver and forming isomorphous mixtures with that constituent. Alloys containing more silver would be, then, isomorphous mixtures. Such conclusion is not in contradiction with the phenomena of crystallization described by Mr. Behrens, for the alloys corresponding to the formulas Ag_6Sn, Ag_4Sn, Ag_3Sn contain more than 70 per cent of silver and would be, therefore, isomorphous mixtures. Ag_2Sn contains about 65 per cent of silver: it would be the definite compound which forms isomorphous mixtures with silver. With regard to AgSn, Ag_2Sn_3, $AgSn_2$, Mr. Behrens himself states the existence of two components unequally fusible: they would correspond to the compound Ag_2Sn and the eutectic alloy.

Alloys of Silver and Zinc. — The curve of fusibility of alloys of silver and zinc, determined by Mr. Gautier, is composed of two branches which meet at a point corresponding to a eutectic alloy with 69 per cent of silver. The branch which starts from the melting-point of zinc is first ascending and exhibits a maximum when the alloy contains about 60 per cent of silver. In the vicinity of this maximum, which seems to correspond to a definite compound, the hardness of the alloys is very great. Moreover, their structure is quite homogeneous, a prolonged etching being necessary to reveal the outlines of some crystals occupying nearly the whole mass.

Alloys rich in silver are composed of crystallites embedded in the eutectic alloy. These crystallites, which in the alloy with 75 per cent of silver are isolated, unite to form dendrites similar to those of bronze, when the alloy contains 80 per cent of silver. One of the best means to develop the

structure consists in treating the sample with sulphuretted hydrogen, which darkens the crystallites. Alloys very rich in zinc are made up of delicate dendrites, having the appearance of fern-leaves and surrounded by a constituent which is readily attacked by caustic potash, but which cannot be further resolved. The constitution of these alloys, therefore, appears to be analogous to that of brasses containing from 0 to 20 per cent of copper.

Conclusions.

The microscopical examination of metals, which gives us a means of studying the treatment to which they were subjected, yields also important informations concerning the chemical constitution of alloys. It gives, so to speak, the proximate analysis of metallic alloys. It shows that the solidification of alloys proceeds like that, more easily observed, of saline solutions, and that binary alloys are generally made up of two constituents only, whatever the number of definite compounds formed by the two allied metals.

The type of normal constitution exhibits, therefore, crystals of an elementary metal or of a definite compound embedded in a second constituent, generally a eutectic mixture, itself made up by the juxtaposition of two minutely divided components, one of which being the same substance as that which makes up the crystals. The composition of the eutectic mixture remains constant, while the proportion of the isolated crystals varies with the ultimate composition of the alloy.

Besides this normal type, which includes the extreme cases corresponding to a pure definite compound or to a pure eutectic mixture, there is only one other type to mention: that of metals forming isomorphous mixtures. Those alloys are made up, whatever their composition, of a single kind of crystals occupying the whole mass, and whose properties and compositions generally vary continuously.

While there is only a small number of metals which form isomorphous mixtures, there seem to be several instances of definite compounds of two metals which form isomorphous mixtures with one of them. From the microscopical examina-

tion of their structure we are led to infer, for instance, the existence of definite compounds of tin and antimony with 50 per cent of tin, of antimony and silver with 20 per cent of antimony, of tin and silver with 30 per cent of tin, which form isomorphous mixtures, the first one with antimony, the last two with silver. The truth of these deductions, however, should be verified by endeavoring to separate these definite compounds.

The constituents of metallic alloys generally form *crystallites* and not well-defined crystals. The form of the constituents, therefore, gives only, in general, approximative information with regard to their nature. They may be recognized, besides, by their color, their hardness, and especially by their behavior when treated with various re-agents.

The mode of preparation and especially the rate of cooling during solidification modifies considerably the dimensions of the crystallites, but does not seem to otherwise influence the constitution of the alloy.

THE CONSTITUTION OF STEEL CONSIDERED AS AN ALLOY OF IRON AND CARBON.*

By ALBERT SAUVEUR.

IT has been conclusively established that in unhardened steel, at least, the totality of the carbon is combined with a portion of the iron forming the carbide Fe_3C, which is then distributed throughout the balance of the iron.† Steel may therefore be considered as a mixture or an alloy of iron and the carbide Fe_3C, and I shall endeavor to show that if we look upon steel in this light, the formation of its structure follows very closely the laws which govern the formation of the structure of a certain class of binary metallic alloys, namely, that group of alloys whose component metals form neither definite compounds nor isomorphous mixtures.

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* Lecture delivered before the Society of Arts of Boston, April 28, 1898. *Technology Quarterly*, June, 1898.

† I purposely ignore here the small amount of graphitic carbon often found in high-carbon steel after annealing.

Great advance has been made in recent years in our knowledge of the true constitution of metallic alloys. Much activity was created in this field of research through the work of special committees organized in England by the Institution of Mechanical Engineers, and in France by the Société d'Encouragement pour l'Industrie Nationale. Among those investigators whose work has been most fruitful, the names of Dr. Guthrie, Roberts-Austen, H. Le Chatelier, Heycock and Neville, Charpy, Gautier and Behrens stand pre-eminent.

The study of the structure of alloys and of industrial metals has even called into existence a new department of science, for the microscope has revealed to us that all alloys and all industrial metals, which always contain a certain amount of impurities, are made up of constituents which may be regarded as minerals, for they possess all the characteristics of true minerals; and as the study of rocks created the science of petrography, so from the study of the constitution of metals and alloys was developed a new department of metallurgy, called metallography.

One of the most brilliant achievements of these recent investigations is to be found in the discovery that the structure of metallic alloys is controlled by the same laws which had been known for some time, to regulate the constitution of mixtures of melted salts and of frozen saline solutions. In other words, the greatest analogy exists between the structure of solid saline solutions and that of metallic alloys. The latter must be considered as true solutions. The fact that they are solid at the ordinary temperature, while saline solutions are liquid, has alone prevented the identity of the laws which govern the formation of the structure of both classes of substances, when they assume the solid state, from being discovered at a much earlier date. With a view of offering a rationale for the constitution of steel I shall briefly recall the working of these laws, although time permits me to do so only in their broadest outline.

Saline Solutions. — We all know that by dissolving common salt, sodium chloride, in water, we lower the freezing-point of the water. By increasing the amount of salt the freezing-point of the resulting mixture is, at first, correspondingly lowered, until it contains a certain percentage of salt.

The lowest possible freezing-point of a solution of sodium chloride in water is then reached, and further addition of salt will gradually raise the freezing-point of the brine.

Dr. Guthrie found that the mixture which has the lowest possible freezing-point contains about 23.50 per cent of NaCl; and as the hydrate containing 10 molecules of water would require 24.50 per cent of salt, Dr. Guthrie inferred that the solution of lowest freezing-point was a hydrate of the formula $NaCl + 10\ H_2O$. He proposed for it and for all similar mixtures, i.e., for all saline solutions of lowest freezing-points,
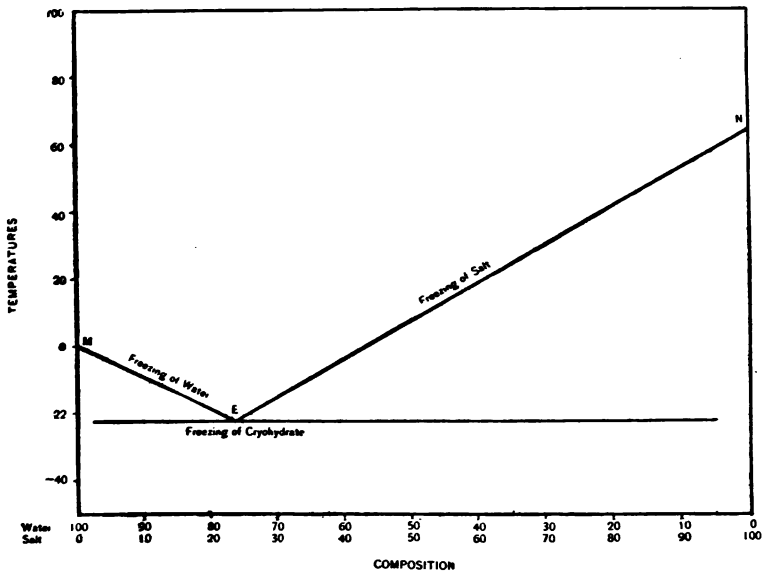
FIG. 1. Curve of Solubility of Aqueous Solutions of NaCl.

the name of *cryohydrate*, by which he meant to imply that they can only exist in the solid state, at a low temperature.

Fig. 1 shows the curve of solubility, or the freezing-curve, which is evidently the same thing, of a solution of sodium chloride in water. The abscisses represent the composition, the ordinates the temperatures at which the various mixtures freeze. The curve is made up of two branches which meet at a point E corresponding to a temperature of — 22° C., and to a solution containing 23.50 per cent of NaCl, i.e., to the composition and freezing-point of the cryohydrate.

Supposing the mixture placed in a proper cooling medium, let us see what happens when a solution poorer in salt than the cryohydrate reaches its freezing-point. It is at that instant saturated with water, and further cooling will cause the *formation of ice*. If a thermometer be placed in the solution it will then indicate a retardation in the rate of cooling which, of course, denotes an evolution of latent heat and marks the beginning of solidification. If the corresponding temperature be plotted on the diagram it will give one point of the branch ME. The formation of pure ice causes the remaining liquid to become richer in salt, and as its freezing-point is thereby correspondingly lowered, the deposition of ice does not take place at a constant temperature, but proceeds as the temeprature is further lowered. The portion remaining liquid meanwhile becomes richer and richer in salt, until at a temperature of − 22° C. it reaches the composition of the cryohydrate. The remaining liquid then solidifies *as a whole and at a constant temperature;* the thermometer placed in the mixture remains stationary until the whole mass has solidified. The heat which is here evolved is the latent heat of solidification of the cryohydrate, and if the corresponding temperature be plotted on the diagram it will give one point of the horizontal line. If the application of cold be continued after the whole mass is solid, the fall of temperature resumes again its normal rate.

A frozen saline solution, then, containing less salt than the cryohydrate, will be made up of crystals of ice surrounded by the frozen cryohydrate. If the solution contains more salt than the proportion found in the cryohydrate, when a certain temperature is reached, the thermometer indicates an evolution of heat which marks the beginning of solidification and corresponds to the formation of *crystals of salt* (sometimes hydrated), for the solution is at that temperature saturated with salt, and further cooling must cause the deposition of salt. The crystals of salt increase in quantity as the temperature continues to fall. The remaining liquid meanwhile becomes correspondingly poorer in salt, approaching more and more the composition of the cryohydrate which it reaches at a temperature of − 22° C. At that instant the portion remaining liquid solidifies as a whole and at a constant tem-

perature, as indicated by the thermometer, which at this stage
remains stationary until the entire mass has solidified. The
plotting of the corresponding temperature gives another point
of the horizontal line. The frozen mass is then made up of
crystals of salt surrounded by the solid cryohydrate. If the
solution has a composition identical to that of the cryo-
hydrate, it will not freeze until it has reached a temperature
of — 22° C., when it will solidify as a whole and at a constant
temperature.

The composition of the cryohydrate, it is seen, is in-
dependent of the composition of the solution, but the propor-
tions of cryohydrate and of ice or of cryohydrate and of salt
found in the frozen solution, depend, of course, upon the
amount of salt in the solution. The branches ME and NE
correspond, therefore, to the *beginning* of the evolutions of
heat which accompany the beginning of solidification of ice
or of salt. Hence they also represent the solubility of salt
in water at various temperatures. The horizontal line cor-
responds to the evolutions of heat corresponding to the solid-
ification of the cryohydrate, and indicates that such solidifica-
tion takes place at a constant temperature, which is the same
whatever the composition of the original solution.

While saline solutions, therefore, containing various pro-
portions of salt *begin* to freeze at temperatures which depend
upon their degree of concentration, they all *finish* freezing at
the same temperature, namely, at — 22° C., the freezing-point
of the cryohydrate.

Seeing that one branch of the curve represents the forma-
tion of crystals of ice in brines poorer in salt than the cryo-
hydrate, while the other branch corresponds to the formation
of crystals of salt in solutions richer in salt, the conclusion is
almost irresistible that their meeting-point must correspond
to a *simultaneous deposition of ice and salt*, and that the frozen
cryohydrate, therefore, must be a mechanical mixture of ice
and salt, probably in an extremely minute state of division,
which would outwardly give it the appearance of a definite
compound; and indeed, Mr. Offer has shown that the cryo-
hydrates do not form distinct and transparent crystals, but
opaque masses, and that alcohol dissolves the ice and leaves
a crystalline net-work of solid salt; also that their heat of dis-

solution is equal to the sum of the heats of dissolution of the ice and of the salt; finally, that the specific gravity is equal to the mean of those of both constituents, which facts argue strongly in favor of the cryohydrates being merely mechanical mixtures of ice and salt.

Mr. Ponsot, moreover, using colored salts, has ascertained that the cryohydrates were actually made up by the juxtaposition of crystals of pure ice and of salt, the salt being sometimes hydrated.* We shall presently find some further evidences that the cryohydrates are merely mechanical mixtures of this description.

What has been said regarding brines applies to all aqueous saline solutions; they all give rise upon cooling to the formation of cryohydrates, i.e., of solutions having a definite composition, and which freeze at a constant temperature which is also the lowest possible in each series.

If we now pass to mixtures of melted salts which form neither definite compounds nor isomorphous mixtures, we find that upon solidifying the formation of their structure is regulated by exactly the same laws. They, too, form a mixture of definite composition and lowest melting-point which solidifies at a constant temperature. Whichever salt is pres-

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* *Recherches sur la Congélation des Solutions aqueuses étendues.* M. H. Ponsot. Paris, 1896.

Mr. Ponsot says: "In order to elucidate this question (the nature of the cryohydrates) I had recourse to microscopical examinations, and to facilitate the observation I used, first, some solutions of colored salts: potassium permanganate, copper sulphate, potassium bichromate. . . .

"In the case of potassium permanganate, as soon as surfusion ceases, *transparent* needles are formed, absolutely colorless, with rectilinear or rounded outlines, and forming arborescent groups: they are made of pure ice. Between these needles is found a colored mass still liquid, but after a few moments and almost suddenly some needles are formed in the middle of the mass, which are intensely colored, very thin and arranged in the shape of fans or of clusters (*faisceaux*): they are crystals of permanganate. The intermediate space between these crystals is colorless. The more rapid the solidification, the smaller the crystals. . . .

"The cryohydrates of Dr. Guthrie do not exist: they are mixtures of pure ice and of a solid salt. The salt may be anhydrous like potassium nitrate, or hydrated like copper sulphate. . . .

"To avoid confusion it is well to suppress the word *cryohydrate*, and to replace it by the word '*cryosel*.'"

ent in excess solidifies first until the composition of the molten mass has reached that of the mixture of lowest melting-point. In these cases the water is simply replaced by another salt; and if we consider water as fused ice, we need not make any distinction between these two classes of substances, namely, between aqueous saline solutions and mixtures of melted salts.

If I have dwelt at such length upon the constitution of frozen saline solutions, it is because it will help us to account for the structure of metallic alloys.

Metallic Alloys. — The present theory of the constitution of alloys so brilliantly worked out classifies all such mixtures into three classes :

     I. Alloys which give neither definite compounds nor isomorphous mixtures.

     II. Alloys which form definite compounds.

     III. Alloys which form isomorphous mixtures.

For our purpose we need only consider the first group, namely, those alloys which form neither definite compounds nor isomorphous mixtures — and to make the matter clearer, let us take an individual instance, that of silver and copper alloys.

Fig. 2 shows what is known as the curve of fusibility of silver and copper alloys. The abscisses represent the composition of the alloys; the ordinates the temperatures at which they solidify. Attention need not be called to the striking resemblance between this curve and that of the saline solution just examined. The former was called a curve of solubility, but solubility and fusibility represent here, obviously, the same phenomenon. Both are freezing-curves. Fusibility applies to mixtures solid at the ordinary temperature; solubility to those liquid at that temperature.

Like the curve of solubility of saline solutions, the curve of fusibility of metallic alloys is obtained by cooling from the molten state mixtures containing various proportions of the two component metals, and by carefully ascertaining, most conveniently by means of a Le Chatelier pyrometer, the temperature at which the cooling is momentarily arrested, or its rate retarded, which indicates an evolution of latent heat and marks the beginning of the solidification of the alloys. As in the case of saline solutions, all alloys of silver and copper,

with one exception, exhibit a second evolution of heat occurring always at the same temperature and corresponding, therefore, to a horizontal line in the diagram.

The curve is composed of two branches starting respectively from the melting-points of pure silver and of pure copper, and meeting at a temperature of 770° C., and for a composition corresponding to 28 per cent of copper and 72 per cent of silver. The mixture of that composition has the lowest possible melting or freezing-point of all silver and copper
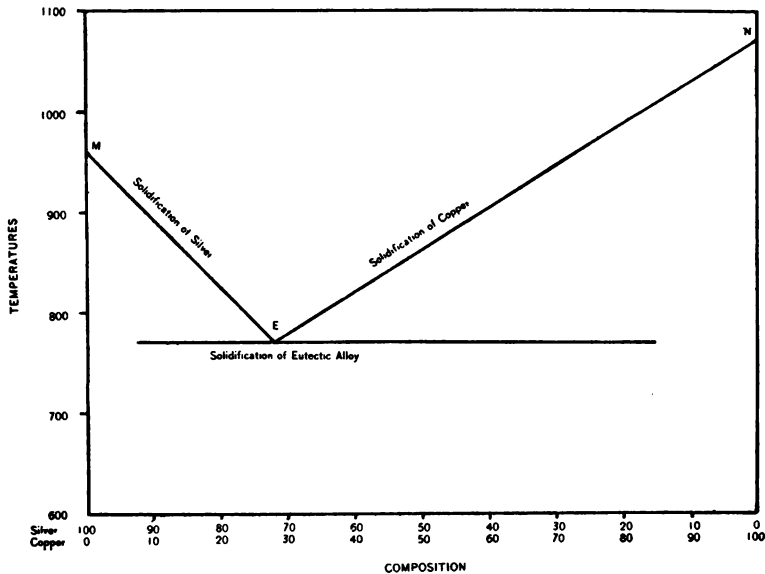
FIG. 2. Curve of Fusibility of Silver and Copper Alloys.

alloys. It is called the *eutectic alloy*, a name proposed for it and for all similar alloys by Dr. Guthrie. It is seen at once that the greatest analogy exists between the eutectic mixtures of metallic alloys and the cryohydrates of saline solutions.

There are two cases to be considered. The composition of the alloy may correspond exactly to that of the eutectic alloy or it may differ from it. In the first case, as the mixture cools from a high temperature, it remains liquid until it reaches the solidification-point of the eutectic alloy, 770° C., when it solidifies as a whole, and at a *constant temperature* as

indicated by the pyrometer, which at this stage remains stationary until the whole mass has solidified. Such a mixture behaves exactly like a saline solution having a composition identical to that of the cryohydrate; the solid mass is made up entirely of the eutectic alloy. See page 17, Fig. 4.*

If the composition of the alloy differs from that of the eutectic mixture, i.e., if one of the constituents is present in excess with regard to that composition, the silver for instance, then when the cooling mass reaches a certain temperature the silver in excess begins to solidify exactly as did the water in the case of a saline solution. This deposition is accompanied by an evolution of heat indicated by the pyrometer, and which, when the corresponding temperature is plotted, gives one point of the branch ME. The separation of pure silver continues until the portion remaining liquid, and which becomes all the while poorer in silver, has reached the composition of the eutectic alloy, 72 per cent Ag + 28 per cent Cu. At that instant the silver is saturated with copper, the copper is saturated with silver, and both metals solidify together at a constant temperature.

Alloys containing a larger percentage of silver than the eutectic mixture will, therefore, be made up of crystalline particles of silver in a matrix of the eutectic alloy. Fig. 5 (page 17) exhibits the structure of an alloy containing 85 per cent of silver. The large black areas represent the pure silver; the composite constituent forming the net-work is the eutectic alloy. The preparation was heated to a purple color, which accounts for the dark appearance of the silver.

If it be the copper which is present in excess with regard to the composition of the eutectic alloy, it is pure copper which begins to solidify when a certain temperature is reached. The solidification of copper continues until the portion remaining liquid has reached a composition identical to that of the eutectic alloy; it then solidifies as a whole and at a constant temperature, which when plotted gives one point of the horizontal line.

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* The photographs which were used to illustrate this lecture have already been published elsewhere in the present volume of *The Metallographist.* The reader will be referred, in every case, to the proper page and figure.

Alloys of silver and copper containing a larger proportion of copper, therefore, than the eutectic mixture, will be made up of crystalline particles of copper surrounded by the eutectic alloy. This is well shown in Fig. 6 (page 17), which represents the structure of an alloy containing 65 per cent of copper, i.e., a large excess of that metal. The large white areas represent the pure copper; the constituent made up of grains or plates alternately light and dark is the eutectic alloy.

What, then, is the nature of these eutectic alloys? Seeing that they always had a definite composition, whatever the composition of the original alloy, and also on account of the closeness of their fractures, which often have a conchoidal appearance, it was thought for many years that they were definite compounds, although their compositions seldom correspond to exact simple ratio of the atomic weights of the components.

On the other hand, seeing that one branch of the curve of fusibility corresponds to the solidification of pure copper, the other to the solidification of pure silver, it would seem highly probable that their meeting-point must correspond to the simultaneous solidification of silver and copper, and that the eutectic alloy is merely a mechanical mixture of the two constituents. The microscope has shown that such, indeed, is the case. All eutectic alloys are made up of extremely minute crystals or plates of the two components in close juxtaposition. This is well illustrated in Fig. 4 (page 17), which shows the structure of the eutectic alloy of silver and copper under a magnification of 600 diameters. Fig. 2 of plate facing page 87, reproduced from a photomicrograph of Mr. Charpy, presents another beautiful instance of the characteristic structure of eutectic mixtures. The component metals are here silver and antimony, and the alloy contains an excess of silver which is represented in the photograph by light areas.*

In the fact that eutectic alloys are mechanical mixtures, we find an additional important evidence that such must also

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* This sample was treated with sulphuretted hydrogen, which blackens the silver while it has no action upon the antimony. The reproduction, however, was prepared from a negative print, so that the silver here appears white instead of dark.

be the constitution of cryohydrates, whose formation is so similar to that of eutectic alloys.

On account of the minuteness of their constituents, eutectic mixtures often require very high power for their resolution, and they frequently present under the microscope a beautiful play of interference colors, strongly suggestive of mother-of-pearl.

Alloys of Iron and Fe₃C. — With the laws which control the formation of the structure of alloys fresh in our minds,
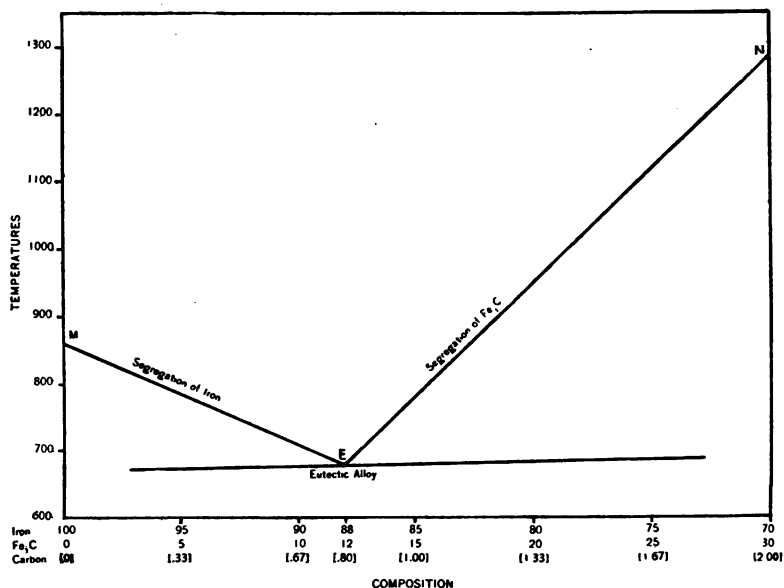
FIG. 3. Curve indicating Evolutions of Heat (accompanied by structural changes) occurring during the Cooling of Steel.

we shall have no difficulty in accounting for the structure of steel as revealed to us by the microscope. In Fig. 3 the abscisses represent the composition of the metal in terms of iron and the carbide Fe₃C, the corresponding percentages of carbon being indicated between brackets. The ordinates represent the temperatures at which some evolutions of heat occur during the undisturbed cooling of the metal.

By allowing samples of steel containing various amounts of carbon to cool from a high temperature, and carefully observing the rate of cooling by means of a Le Chatelier pyrom-

eter, when a certain temperature is reached, which varies with the carbon-content, a sudden retardation occurs which denotes, of course, some evolution of heat. By plotting the corresponding temperatures, the curve MEN is obtained. The diagram also indicates that on further cooling a second evolution of heat occurs, this time at nearly the same temperature, whatever the degree of carburization of the metal. Graphically, therefore, it is represented by a nearly horizontal line.* This second evolution of heat is generally very marked. It is sometimes so intense as to produce an actual rise in the sensible temperature of the steel, a "recalescence" of the cooling metal. It is why the phenomenon is known by the name of recalescence, and the temperature at which it occurs called the temperature or the point of recalescence. It is a critical temperature of vital importance; in passing through it the structure of the steel is entirely changed, and nearly all its properties, chemical, physical and mechanical, markedly altered.

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* The temperatures at which retardation occurs during the cooling of steel do not, of course, when plotted, give absolutely straight lines; experimental errors alone would preclude such possibility. Moreover, slight amounts of impurities have a notable influence upon the position of the retardation, and it is quite impossible to obtain various grades of steel absolutely free from impurities or containing exactly the same amount. It is sufficient for our reasoning that the curve should be made up, as it is, of two branches which meet in the region indicated. The two branches appear not to deviate very much from straight lines, and might possibly coincide exactly with them if experimental errors and other disturbing factors could be eliminated. It should also be stated that these evolutions of heat do not begin and end at the same temperature, but, on the contrary, cover a noticeable range — sometimes as much as 50° C. or more — so that the first and second evolutions run together long before a carbon-content of 0.8 per cent has been reached, with the result that steel containing over 0.50 per cent carbon appears to have only one retardation extending over a considerable range of temperature: the end of the first retardation merges into the beginning of the second.

Finally, when the metal contains less than about 0.25 per cent carbon, a third retardation is detected, located between the first evolution and the point of recalescence. It has been purposely left out of this diagram, because it would have rendered the resemblance which the latter bears to the curve of solubility or of fusibility just examined, less marked, and to little purpose, for the existence of a third evolution of heat confined to these narrow limits does not sensibly affect the strength of the deduction drawn from the striking analogy of the curves.

The appearance of the diagram obtained in this way recalls at once the curve of solubility of saline solutions and that of fusibility of metallic alloys.   Here again we have two branches of curves, meeting in this case at a temperature of about 670° C., and for a composition corresponding to 12 per cent of Fe_8C (or 0.8 per cent carbon) in the steel.   We have also a nearly horizontal line passing by the point of intersection.   The analogy between the three curves (Figs. 1, 2 and 3) is, indeed, so striking that it will readily suggest, I believe, the inference that the branch ME (Fig. 3) corresponds to the separation or segregation (we cannot use the word solidification here, for at this temperature the whole mass is solid) of the iron, and the branch NE to the segregation of the carbide Fe_8C, while the point E marks the formation of a eutectic alloy of iron, and Fe_8C, i.e., a mechanical mixture whose structure should be made up of small crystalline plates or grains alternately of iron and Fe_8C, and resulting from the simultaneous segregation of the two constituents.   If we are right, steel containing less than 12 per cent of Fe_8C (0.8 per cent carbon) should be made up of crystalline grains of pure iron (at least of carbonless iron) surrounded by the eutectic alloy of Fe and Fe_8C; steel more highly carbonized should be formed of grains of the carbide Fe_8C surrounded by the eutectic alloy, while if the metal contains exactly 0.8 per cent carbon it should be entirely made up of the eutectic alloy.

Such conclusions are confirmed in every particular by the microscopical examination of the structure of various grades of steel.   Figs. 8 and 9 of plate facing page 1, and Fig. 7 (page 21) show the reproduction of some beautiful photomicrographs taken by Mr. Osmond under a magnification of 1000 diameters.   Fig. 8 exhibits the structure of the eutectic alloy of Fe and Fe_8C.   It presents all the structural characteristics of eutectic mixtures, being made up of thin plates alternately of Fe and Fe_8C.   These plates seldom exceed $\frac{1}{40000}$ of an inch in thickness; the plates of iron are somewhat darkened (or rather deprived of their metallic luster) by the polishing and etching, while the plates of Fe_8C are left white and brilliant, and stand slightly in relief.   The arrangement is, therefore, similar to that of the reflection gratings of physicists, and explains the pearly appearance of this remarkable constituent.
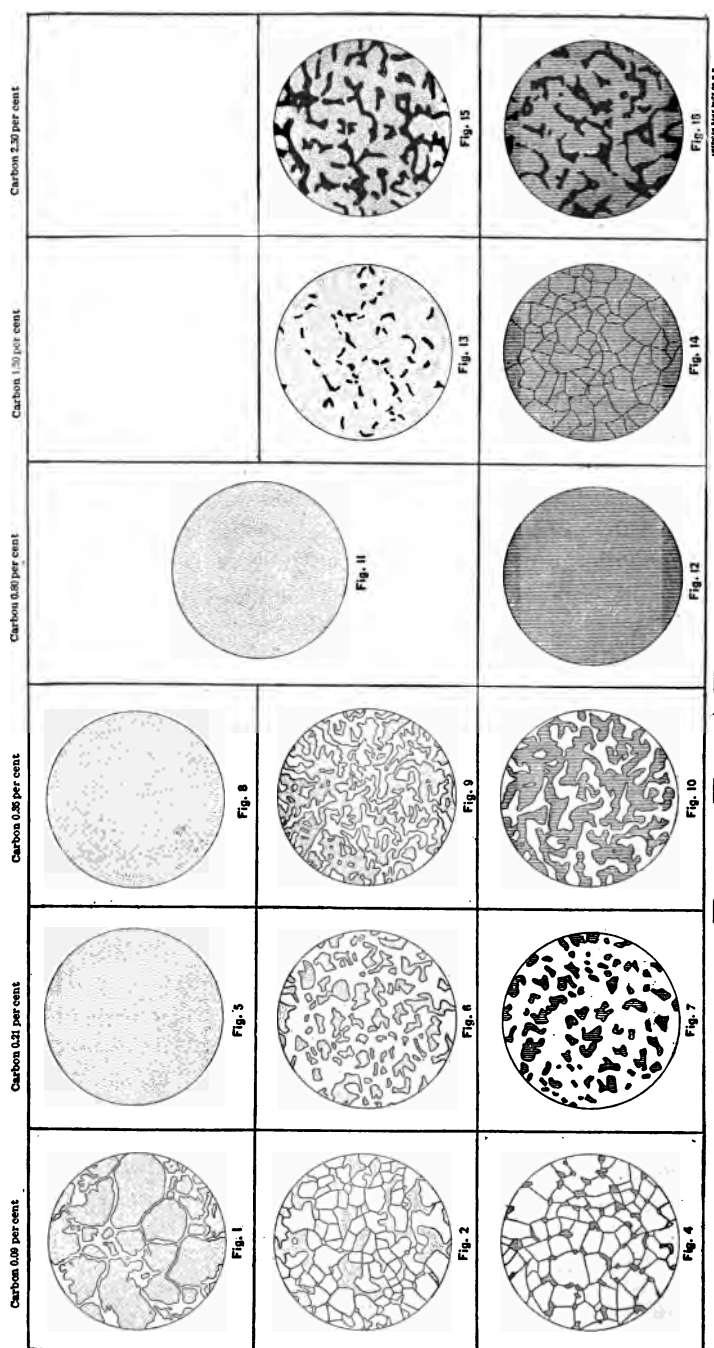
The steel of Fig. 9 of the same plate contains 1.50 per cent of carbon, therefore an excess of Fe_3C with regard to the composition of the eutectic alloy. The white portion standing in relief represents areas of Fe_3C. It is surrounded by the eutectic alloy. Fig. 7 (page 21) shows the structure of a steel containing less carbon, and therefore more iron, than the eutectic mixture. The light background indicates the excess of iron. The accuracy of the deductions drawn from the appearance of the curve of Fig. 3 is further illustrated by the lowest row of drawings of Plate I, which shows the structure of a series of slowly cooled steels of ascending carbon-content. They were drawn directly from the microscope under an original magnification of 250 diameters reduced in the reproduction to 72 diameters. The shaded constituent represents the eutectic alloy; the pure iron has been left white, which is its appearance under the microscope; while the carbide Fe_3C is here represented by black areas to distinguish it more readily from the iron, although in reality it has a brilliant, metallic appearance.

Mineralogical names have been given to these constituents : Pure iron has been called *ferrite*. The carbide Fe_3C, *cementite*, because abundant in cement-steel, while the name of *pearlyte* has been given to the eutectic alloy of Fe and Fe_3C, i.e., of ferrite and cementite, because of its pearly appearance.* The composition of pearlyte, like that of any eutectic alloy, remains the same, whatever the composition of the steel, i.e., whatever its carbon-content. It always contains in the neighborhood of 0.8 per cent of carbon.† The relative proportions of ferrite and pearlyte, however, or of cementite and pearlyte in the steel, vary, of course, according to the degree of carbonization.

Very low carbon-steels, then, are made up of a matrix of iron or ferrite, with here and there a particle of pearlyte

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* These very appropriate names were suggested by Professor Henry M. Howe, and have been quite universally adopted.

† Professor Arnold experimenting with exceptionally pure carbon-steels, especially prepared, finds that pearlyte contains nearly 0.9 per cent carbon. In the case of commercial steel, however, the carbon-content of pearlyte is nearer 0.8 per cent. Impurities, and it would seem especially manganese, have a tendency to lower the percentage of carbon in pearlyte.

PLATE I. Microstructure of Steel.

(Plate I, Fig. 4); the fine black lines indicate the junction lines between the grains of ferrite. As the carbon increases, the amount of pearlyte increases proportionally (Plate I, Figs. 7 and 10), until with 0.8 per cent of carbon the metal is made up entirely of pearlyte (Plate I, Fig. 12). It is then said to be saturated. With further increase of carbon, cementite makes its appearance, increasing in quantity with the carbon-content, causing, of course, a corresponding decrease in the amount of pearlyte (Plate I, Figs. 14 and 16).

The structural composition of any carbon-steel may readily be calculated from its carbon-content. If the steel contains less than 0.8 per cent of carbon it is made up of ferrite and pearlyte. Let x be the percentage of ferrite, y that of pearlyte; we have

$$(1) \quad x + y = 100$$

and since the totality of the carbon is found in the pearlyte and forms 0.8 per cent of its composition, we have the second equation :

$$(2) \quad \frac{0.8}{100} y = C$$

in which C represent the known amount of carbon in the steel.

If the metal contains more than 0.8 per cent carbon, it is composed of pearlyte and cementite. If z be the percentage of cementite, we have

$$(1) \quad y + z = 100.$$

Pearlyte contains 0.8 per cent C, and cementite 6.67 per cent C (which is the proportion required by the formula Fe_3C), and since the sum of the pearlyte-carbon and of the cementite-carbon must be equal to the total carbon in the steel, we have the second equation :

$$(2) \quad \frac{0.8}{100} y + \frac{6.67}{100} z = C.$$

While the similarity between the formation of the structure of alloys or of frozen saline solutions and that of carbon-steel is indeed striking, there is one feature in which the two phenomena differ, which is momentous. In the case of alloys or of saline solutions the curves of fusibility or of solubility, which indicate the temperature at which the constituent pres-

ent in excess begins to segregate from the mass, also represent the beginning of the *solidification* of that constituent. The heat evolved is a latent heat of solidification. It indicates a change of internal energy *accompanied by a change of state.*

In the case of steel, on the contrary, the whole metallic mass is already in the solid state when segregation of the constituents takes place. The heat evolved here indicates a change of internal energy which is *not accompanied by a change of state.* A change of this kind is of course very suggestive, if not conclusive, of an allotropic transformation, and in it the believers in the allotropy of iron find their strongest argument.

Such considerations lead us to the notion of solid solutions. The existence of solid solutions can no longer be reasonably contested. We all know with what readiness carbon diffuses through solid steel. The phenomenon is in every way similar to the diffusion of salt in water. Many instances of solid solutions — diffusions of one metal in another, etc. — have been described recently by Prof. Roberts-Austen and others.

The constitution of steel, before the segregation of one of the components has begun, i.e., above the curve MEN (Fig. 3), remains to be ascertained. This region evidently corresponds to the liquid state in metallic alloys and in saline solutions, from which it might naturally be inferred that the carbide Fe_3C is here uniformly diffused or dissolved through the iron.

It is hardly possible to examine the structure of the metal at a red heat, but by cooling the steel from one of these high temperatures very rapidly — by immersing it in cold water or in some other cooling mixture — the changes, structural and others, 'which take place during the retardations, do not occur, at least not in their entirety (being denied the necessary time), and we retain in the cold metal the conditions which existed at a high temperature. Such treatment constitutes the process of *hardening*, and we must ascertain the character of the constitution of *hardened* steel.

Calling the microscope to our assistance, we find that if the metal be quenched before the first retardation, unless it be very slightly or very highly carbonized, it is made up of a

single constituent represented by dotted areas in the figures of Plate I, and which has been called *martensite*. Figs. 5, 8 and 11 illustrate the structure of steels containing respectively 0.21, 0.35 and 0.80 per cent of carbon, and quenched above the curve MEN (Fig. 3). Fig. 10 (page 23) shows the structure of martensite under a magnification of 1000 diameters. It is the reproduction of a photomicrograph by Mr. Osmond. If the metal contains very little carbon, a small amount of iron (ferrite) is found together with the martensite, even after quenching from a very high temperature. See Plate I, Fig. 1. In highly carbonized steel Mr. Osmond finds, upon sudden cooling from a high temperature, a new constituent which he has named *austenite*. Fig. 11 (page 23) shows the structure of a steel containing 1.50 per cent carbon and quenched in ice-water from a very high temperature (1050° C.). The light background represents the austenite; the dark needles are made up of martensite. If the metal be quenched between the first and the second evolutions of heat, it is found to be made up of a mixture of martensite and ferrite, or of martensite and cementite; the former when the metal contains less than 0.8 per cent carbon, the latter when more highly carbonized. This is well illustrated by Figs. 2, 6, 9, 13 and 15 of Plate I. In steels quenched below the recalescence temperature no martensite is to be found. Their microstructural compositions do not differ from those of the slowly cooled metals (Plate I, lowest row), and we know that steel suddenly cooled from a temperature below that of recalescence is not materially hardened, if at all.

We all know that within certain carbon limits the most striking difference between the properties of steel suddenly cooled from a high temperature, and those of the same metal slowly cooled, is to be found in the enormously greater mineralogical hardness of the former. This increase of hardness it evidently owes to the presence of martensite. The statement, however, does not in any way help us to solve the problem of hardening, which has been the subject of so much investigation and so much controversy, for the cause of the hardness of martensite remains to be determined.

Martensite may be compared to the liquid portion of saline solutions and of metallic alloys. Above the curve

MEN (Figs. 1 and 2) the former are entirely liquid, while steel is made up entirely of martensite (with the exceptions noted above). Between the first and the second evolutions of heat we have in the one case crystals of one of the constituents suspended in the portion remaining liquid; in the other, crystalline particles of ferrite or of cementite embedded in a matrix of martensite; while below the second retardation no portion of the saline solution or of the alloy remains liquid, and no martensite remains in the steel.

It is certainly reasonable to suppose that martensite is a homogeneous solid solution of carbon or of the carbide Fe_3C in iron. It can hardly be anything else. The contention that it is a definite compound of iron and carbon (to which Prof. Arnold would give the formula $Fe_{24}C$) must be abandoned, for it is evident that its composition, like that of the portion remaining liquid during the cooling of metallic alloys, varies both with the composition of the steel and with the temperature.

The fact, however, even if it were conclusively established, that martensite is a solution of iron and carbon or of iron and Fe_3C, could hardly account for its extreme hardness, although certain metallurgists, the "carbonists" as they have been called, see in it a satisfactory explanation of the hardening of steel. The theory of the "allotropists," who consider martensite as a solution of carbon or of Fe_3C in an allotropic condition of the iron, itself very hard, is more plausible; it is supported by much more cogent evidences, and is steadily gaining ground.

While unhardened steel is generally made up of two of the three constituents, ferrite, cementite and pearlyte, it may be readily conceived, however, that even if no other impurities were present, the physical properties of the steel, which give to this metal such a unique place in the arts, do not depend exclusively upon the relative proportions of these constituents — in other words, upon the carbon-content; but that they depend also upon the distribution, mode of occurrence, size and shape of the individual grains or crystalline particles, and these features are regulated by the treatment, thermal and physical, to which the metal is subjected.

The structure of steel is extremely sensitive to slight

changes of treatment, and an alteration of the structure, however slight, always implies a corresponding alteration of physical properties.

The microscope gives us a means of studying those structural changes which are so closely related to the properties of the metal, and thus opens up possibilities in the art as well as in the science of metallurgy, whose value could hardly be overestimated.

MAGNETIC PROPERTIES OF HARDENED STEELS.

By Mrs. SKLODOWSKA CURIE.

Magnetic Properties of Quenched Steel Bars.

INFLUENCE OF THE CHEMICAL COMPOSITION.

THE coercitive field H_c and the intensity of residual magnetization I_r of quenched steel bars from various sources and of various composition will be found in Table IV. Each steel bar was quenched under the conditions which had been found the most desirable for that particular kind and grade of steel, so that the quenching temperature is not the same for each sample. All the bars were 20 cm. long; many of them had a cross-section 1 cm. square. Unfortunately, some bars had different sections. The intensities of residual magnetization corresponding to the bars which did not have the same section are tabulated in separate columns. The figures in the same column are, therefore, comparable. The last column contains the intensity of residual magnetization I' for a closed circuit, found in the case of the few samples which were examined in the form of rings. Some bars of Firminy steel containing 0.84 per cent carbon, and of various sections, were used as standards for the comparison of bars of similar section.

The coercitive field of the bars is almost independent of their dimensions, and is nearly the same as the coercitive field of a closed circuit. The intensity of residual magnetization in the case of a bar, on the contrary, is a complex quantity

TABLE IV. — *Magnetic Properties of Steel Bars of Various Composition.*

KIND	BRAND		%C.	T	Hc	I₁	I₂	I₃	I₄	I'
Carbon-steels	Firminy		0.06	1000	3.4	30	—	—	—	625
			0.20	850	11	120	—	—	—	770
			0.49	770	23	220	—	—	—	835
			0.84	770	53	420	—	480	580	640
			1.21	770	60	460	—	—	—	645
	Boehler Styria	Soft	0.70	800	49	420	—	—	—	—
		Medium-hard	0.96	800	56	420	—	—	—	—
		Extra tenacious-hard	0.99	800	55	410	—	—	—	—
		Extra medium-hard	1.17	800	63	460	—	—	—	—
			1.13	850	65	420	—	—	—	—
	Unieux		0.75	770	51	410	—	—	—	—
			0.80	770	53	420	—	—	—	—
			0.83	770	56	440	—	—	—	—
			0.96	770	58	430	—	—	—	640
			1.40	750	61	—	500	—	—	—
			1.41	750	61	—	500	—	—	—
			1.61	750	46	—	370	—	—	—
Boron-steels	Châtillon and Commentry	% Bo. *a* ?	0.7?	800	26	250	—	—	—	—
		b 0.5	1.05	800	44	410	—	—	—	—
		c 0.8	0.97	800	51	430	—	—	—	—
Chromium-steels	Assailly	% Cr. C₁ 2.5	0.50	900	45	460	—	—	—	—
		C₂ 2.8	0.82	900	56	500	—	—	—	—
		C₃ 3.4	1.07	850	57	530	—	—	—	—
Copper-steels	Châtillon and Commentry	% Cu. 3.9	0.87	730	66	490	—	—	—	—
Tungsten-steels	Assailly	% W. V₁ 2.9	0.55	850	51	460	—	—	—	800
		V₂ 2.7	0.76	850	66	510	—	—	—	—
		V₃ 2.7	1.10	830	68	500	—	—	—	—
	Châtillon and Commentry	*a* 3.2	0.77	800	65	550	—	—	—	—
		b 2.7	1.02	800	69	540	—	—	—	—
		c 3.5	1.53	1000	50	320	—	—	—	—
	Boehler Styria	Special very hard 2.9	1.10	850	74	530	—	—	—	—
		Boreas unhardened 7.7	1.96	800	45	350	—	—	—	—
		Boreas hardened 7.7	1.96	800	85	370	—	—	—	—
	Allevard	5.5	1.59	770	72	560	—	—	—	—
		5.5	0.59	770	74	—	680	—	—	850
Molybdenum-steels	Châtillon and Commentry	% Mo. A 3.5	0.51	850	60	530	—	—	—	—
		B 3.4	1.25	800	82	480	—	—	—	—
		B 4.0	1.24	800	85	530	—	—	—	—
		C 3.9	1.72	770	73	510	—	—	—	—
		3.9	1.72	830	79	415	—	—	—	—
		3.9	1.72	800	78	560	—	—	—	—
Nickel-steels	Fourchambault	% Ni. Ni₁ 3.6	0.57	730	55	—	—	490	—	—
		Ni₂ 3.0	0.70	730	48	—	—	535	—	640
		Ni₃ 3.7	1.21	730	48	—	—	480	—	—
Manganese-steels	Fourchambault	% Mn. A 0.7	0.46	780	32	—	—	380	—	860
		B 1.8	1.18	780	64	—	—	500	—	—
		C 2.2	1.94	780	55	—	—	440	—	—
		AL 0.3?	0.9?	780	52	—	—	380	—	—
		BL 0.6?	0.9?	780	55	—	—	410	—	—
		CL 0.9?	0.9?	780	54	—	—	390	—	—
	Hadfield	Annealed 13.0?	1.0?	—	135	—	—	—	70	—
		Hardened 13.0?	1.0?	830	?	—	—	—	0	—
Silicon-steels	Châtillon and Commentry	% Si. I 0.11	0.91	780	54	—	—	—	660	—
		II 0.64	0.91	780	50	—	—	—	660	—
		III 1.28	0.72	780	34	—	—	—	815	—

Length of all the bars, 20 cm. — T = hardening temperature. — Hc = coercitive field.
I₁ = intensity of residual magnetism for a section 1 cm. square; I₂, for 0.85 cm. square; I₃, for 1 cm. in diameter; I₄, for 0.5 cm. in diameter; I', for a closed magnetic circuit.

which depends upon the residual intensity of a closed circuit, the coercitive field and the shape of the bar. The intensity of residual magnetization of the bars which have been studied is altogether different from that which would result from a closed circuit. (See Table IV.) The influence of the value of the coercitive field is, generally, predominant, and the intensity of residual magnetization of the bar varies in the same direction as the coercitive field; if, however, these bars, which have a very high coercitive field (tungsten or molybdenum steel), are compared with each other, it is seen that the intensity of residual magnetization differs less from the one obtained with a closed circuit, and that the influence of the latter becomes more marked; the coercitive field and the residual magnetization of the bars do not, in that case, vary any longer in the same direction.

The magnetic qualities of a steel cannot be judged from a mere comparison of the intensities of residual magnetization exhibited by bars of same dimensions. Conclusions altogether different would, indeed, be reached by varying the dimensions of the bar adopted for these experiments; such conclusions might even be reversed.

Carbon-steels. Influence of the Percentage of Carbon. — The highest values for the coercitive field and the intensity of magnetization ($H_c = 62$; $I_r = 460$ for bars 20 $\times$ 1 $\times$ 1 cm.) have been obtained in the case of bars containing in the neighborhood of 1.1 or 1.2 per cent of carbon. It should be noted that the Unieux steels are the purest; those of Firminy, which contain only 0.2 per cent of manganese, come next. (See Table I, page 119.)

Boron-steels. — The boron-steels placed at my disposal contained only very small amounts of that element (0.5 and 0.8 per cent). Their magnetic properties are comparable to those of pure carbon-steels containing the same percentages of carbon.

Silicon-steels. — Three bars only were examined. The presence of small quantities of silicon does not appear to modify sensibly the magnetic properties.

Nickel-steels. — The presence of 3 per cent of nickel' does not modify very much the magnetic properties; still, the sample of nickel-steel slightly carburetted (0.5 per cent C)

has a coercitive field (55) higher than that of carbon-steels containing the same amount of carbon. The nickel-steels which have been examined should not be quenched at a high temperature, their magnetic qualities diminishing rapidly as the quenching temperature increases.

Manganese-steels. — The magnetic properties of manganese-steels containing less than 2 per cent of manganese do not differ much from those of carbon-steels of same carbon-contents.

The manganese-steel of Hadfield, containing 13 per cent of manganese, possesses, as is well known, very peculiar properties. In the quenched condition it cannot be magnetized; at least the intensity of residual magnetization of the bars is not observable by means of the apparatus used in the present investigation, and, consequently, neither can their coercitive field be determined.

In the annealed condition, on the contrary, the steel bars can be magnetized; the intensity of residual magnetization is then very feeble and the coercitive field very high.

Chromium-steels. — The samples examined contained from 2.5 to 3.5 per cent of chromium. Chromium, like nickel, increases the coercitive field and the intensity of magnetization of the least carburetted samples (0.5 and 0.8 per cent C). In the case of chromium-steel with 1 per cent of carbon, the presence of chromium raises only the value of the residual intensity.*

Copper-steels. — The sample examined contained 4 per cent of copper and 0.9 per cent of carbon. The presence of copper improves the magnetic properties.

Tungsten-steel. — The magnet-steels actually used for the construction of physical instruments are tungsten-steels. The presence of this element increases the coercitive field and the intensity of residual magnetization of the bars, whatever the carbon-content. The coercitive field of the very highly carburetted sample of Commentry steel, containing 1.50 per cent of carbon, is not increased, however, by the presence of 3.5 per cent of tungsten. Among the tungsten-steels which have

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* It should be stated here that the analysis of the chromium-steels revealed the presence of a portion of the carbon in the graphitic state, or, at any rate, in a condition in which it is insoluble in acids.

been studied, those possessing the best qualities for the con-
struction of magnets may be divided in two classes : (1) steels
containing 3 per cent of tungsten and a large amount of
carbon (1.1 per cent C), such as the following samples :
Assailly steel V_s, *Commentry* steel (*b*) and *very hard special
Boehler* steel ($H_c = 74$; $I_r = 530$); (2) steels containing a
smaller percentage of carbon (0.6 per cent C), but with 5.5
per cent of tungsten, such as the *Allevard* sample ($H_c = 72$;
$I_r = 560$).

The very hard special Boehler steel yielded very different
results according to the hardening conditions. Heated a long
time previous to quenching, its magnetic qualities were found
to have diminished. Bars of this steel sometimes broke after
quenching.

The Allevard steel is not so easily spoiled during heat-
ing, but it is also liable to crack upon quenching. Between
740° and 825° C. the quenching temperature has no appreciable
influence upon the magnetic properties of the bars. It is,
however, preferable to heat the metal to a relatively low tem-
perature in order to avoid cracking the steel on quenching.
By quenching from a temperature of 850° or higher, the
resulting magnets are not as good. Heating to 900° is in-
jurious, even if the steel is then quenched at a lower tem-
perature. Prolonged heating (one hour) at 780° does not
alter, in an appreciable degree, the properties of the steel.

The nature of the quenching-bath was also varied in the
case of the Allevard steel. Hardening in a freezing mixture,
at − 18° C., gives the same results as hardening in water, at
+ 15°. Quenching in mercury, on the contrary, is more
effective than water quenching, but it was only possible to
apply it to very small bars. In order to quench a large piece
it would be necessary to have a bath of considerable size, so
as to avoid too great a heating of the mercury. The results
obtained with the small bars of Allevard steel, measuring
9.3 cm. in length and having a section 0.5 cm. square, are as
follows :

Bars quenched in water   .   . $H_c = 73$ $I_r = 550$
Bars quenched in mercury .   .· $H_c = 78$ $I_r = 540$.

The coercitive field is remarkably intense after quenching in
mercury.

Less sudden coolings than that produced by cold water being frequently resorted to in order to avoid cracking, I have endeavored to ascertain the effect of those milder treatments upon the magnetic properties of Allevard steel. Quenching in oil is insufficient. Quenching in water covered with a layer of oil gave more satisfactory results, but the magnetic qualities were then reduced to those of a good carbon-steel quenched in water. It is possible that, by placing on the water a thinner layer of oil, a satisfactory working condition might be found which would not entail too great a loss of the magnetic properties.

The Commentry tungsten-steel, with 1.53 per cent of carbon and 3.5 per cent of tungsten, is not a good steel for magnets. It should be noted that, in spite of its high percentage of carbon,[*] this steel is improved, with regard to its magnetic properties, by being quenched at a high temperature. When quenched at 750°C., for instance, $H_c = 34$ and $I_r = 315$; at 850° C., $H_c = 35$ and $I_r = 318$; when quenched at 900°, $H_c = 39$ and $I_r = 340$; and after quenching at 1000°, $H_c = 50$ and $I_r = 320$.

The properties of the Boehler steel marked *Boreas* are very curious. This steel contains a large proportion of tungsten : 7.7 per cent, a very large amount of carbon : 2 per cent, and 2 per cent of manganese. When slowly cooled in the air (air-quenched), this metal possesses the properties of ordinary steels quenched in the usual way, and it is in this condition that it is used for tools. A steel bar after such treatment is already susceptible of being strongly magnetized ($H_c = 45$, and $I_c = 350$ for a bar measuring $20 \times 1 \times 1$ cm.). Its magnetic properties are improved by quenching in water ($H_c = 85$, $I_r = 370$). This special steel, therefore, when quenched in water, possesses a considerable coercitive field, but its intensity of magnetization is weaker than that of bars of same dimensions of the other tungsten-steels. Short and thick bars of Boreas steel would probably yield stronger magnets than those constituted by similar bars of other tungsten-steels. Boreas steel is not homogeneous and is difficult to work. The results obtained with various bars, after quench-

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[*] This sample contained 0.35 per cent of carbon insoluble in acids.

ing, are not concordant; some bars gave a coercitive field much weaker and a greater intensity of residual magnetization ($H_c = 68$ and $I_r = 430$, for instance).

Molybdenum-steel. — Of all the steels which have been examined, molybdenum-steel is the best for the construction of magnets. This steel is not yet commercially used. The presence of from 3.5 to 4 per cent of molybdenum improves decidedly the magnetic qualities of the steel, whatever the percentage of carbon; even when as large an amount as 1.7 per cent of carbon is present. With 1.25 per cent carbon, $H_c = 85$, $I_r = 530$, with 1.72 per cent carbon, $H_c = 78$, $I_r = 560$ in the case of bars $20 \times 1 \times 1$ cm. With an intensity of magnetization similar to that of tungsten-steels, they have a much greater coercitive field. The bars sometimes crack on quenching. As the quenching temperature is increased, the intensity of magnetization decreases, but the coercitive field remains stationary or increases. One of the bars containing 1.72 per cent of carbon gave, for instance, the following values:

<pre>
Bar quenched at 745° C.   .   .   Hc = 73   Ir = 465
Bar quenched at 830° C.   .   .   Hc = 79   Ir = 415
Bar quenched at 890° C.   .   .   Hc = 76   Ir = 300.
</pre>

General Remarks on the Influence of the Chemical Composition upon the Magnetic Properties of Steel. — Among pure carbon-steels, those which give the best magnets contain about 1.2 per cent of carbon. The presence of a little boron, silicon or manganese, does not seem to have any appreciable influence. Nickel, chromium and copper improve the magnetic qualities of steel. Finally, the tungsten-steels and the molybdenum-steels are the best for the construction of magnets. It is somewhat remarkable that the metals whose influence is relatively slight, such as nickel and chromium, modify more those steels which are only slightly carburetted, while the more powerful elements improve the magnetic qualities of all steels, whatever their carbon-content. The presence of molybdenum or of large quantities of tungsten impart, even, remarkable qualities to steels which contain a very large amount of carbon (1.7 to 2 per cent C). By comparing a molybdenum-steel (such as the sample B, Table IV, for instance) to a tungsten-steel, such as the Allevard sample, it is seen that,

in the case of bars having the dimensions indicated, the intensity of magnetization is similar.   As the coercitive field of the molybdenum-steel is greater, it is very probable that, in the case of a closed circuit, the residual intensity of that steel is, on the contrary, less than that of the Allevard steel.   It follows, therefore, that the magnets which form closed or nearly closed circuits will be more intense, if made of Allevard steel, while, on the contrary, open magnets or short bars will have a greater intensity if made of molybdenum-steel. In any case, the stability of the magnetism will be greater with the molybdenum-steel B.*

The molybdenum-steel A, on the contrary, possessing in the shape of a bar a high intensity of magnetization with a coercitive field weaker than that of the Allevard steel, would probably have, in a closed circuit, an intensity of magnetization greater than that of the Allevard metal, with less stability of magnetism.

To sum up, the influence of tungsten appears to be analogous to that of molybdenum, but a larger proportion of the former is probably required to produce the same effect.   It would seem, however, that molybdenum-steel is able to carry a larger percentage of carbon without detrimental effect.

Intensity of the Mean Magnetization of the Bars. — The mean magnetization has been ascertained only in the case of a few bars.   The ratio $\dfrac{I_m}{I_c}$ of the mean intensity of magnetiza-

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* The following experiment may be imagined : prepare three horse-shoe magnets widely open, of the same shape, but respectively of carbon-steel with o.5 per cent carbon, of Allevard steel and of molybdenum-steel B. The magnets being first provided with soft iron armatures, so as to constitute magnetic circuits nearly closed, each magnet is magnetized by means of a current circulating around it, and after a few moments the current is suppressed.   Under these conditions, the magnets made of carbon-steel and of Allevard steel are equally powerful, and will have a carrying force greater than that of the molybdenum magnet.   If the armatures are removed, it is, on the contrary, the molybdenum-steel which will remain the most intensely magnetized ; the Allevard magnet will come next, while the carbon-steel magnet will have lost the greatest part of its magnetization. After replacing the armatures, the molybdenum magnet will retain its superiority and will have a carrying force greater than that of the Allevard magnet ; the carrying force of the carbon magnet will be very weak.

tion I_m to the intensity I_c at the center of the bar gives *the ratio of the distance of the poles to the length of the bar.*

The figures of Table V all refer to bars 20 cm. long with a section 1 cm. square, which have been magnetized to saturation.

TABLE V. — *Intensity of the Mean Residual Magnetization.*

		I_c	I_m	$I_m|I_c$	H_c
Carbon-steels	C = 0.49 per cent	188	143	0.76	22
	C = 0.84 per cent	376	294	0.78	50
Tungsten-steels (Assailly)	V_1	413	298	0.72	42
	V_2	514	403	0.78	65
	V_3	420	345	0.82	66
Molybdenum-steels, mild quenching (Châtillon and Commentry)	A	590	450	0.76	74
	B	432	363	0.84	63
Allevard steel	I	541	435	0.80	73
	I	544	427	0.78	72
	III	557	444	0.80	—
	IV	520	417	0.80	—
	V	572	458	0.80	—

The ratio $\dfrac{I_m}{I_c}$ are included within comparatively narrow limits: 0.72 and 0.84, their value for the most part being in the neighborhood of 0.80. There is apparently no simple relation between this ratio, the intensity I_c and the coercitive field H_c. It seems probable that the ratio $\dfrac{I_m}{I_c}$ depends both upon the coercitive field and the intensity of magnetization at the center of the bar. It is probable that the tendency of this ratio is to increase with the coercitive field, and to diminish when the intensity of magnetization increases.

CLOSED MAGNETIC CIRCUITS.

The following steels were studied in the shape of closed magnetic circuits:

A series of five carbon-steels from the Firminy steel-works, with ascending carbon-content, a carbon-steel from Unieux, the Allevard steel, a tungsten-steel V_2 from the Assailly works, a steel with 3 per cent of nickel, and one with 0.7 per cent of manganese.

A few interesting brands of steel are found missing in this investigation. A ring of special Boehler steel (very hard)

TABLE VI. — *Closed Magnetic Circuits.   Cycles of Magnetization.*

BRAND AND KIND	ASCENDING BRANCH		DESCENDING BRANCH	
	H.	I.	H.	I.
FIRMINY Carbon-steel C = 0.06 %	3.5	36	505	1560
	4.2	181	256	1495
	5.5	350	167	1440
	8.3	685	78.5	1330
	21.0	925	42	1220
	52.8	1190	16.1	980
	135.5	1400	0	625
	258	1490	— 1.8	480
	—	—	— 2.5	293
	—	—	— 2.9	113
	—	—	— 3.2	0.8
C = 0.20 %	7.7	36.5	505	1590
	11.4	340	490	1580
	23.6	825	248	1500
	56.0	1200	162	1450
	84.5	1300	76.8	1320
	120.5	1350	0	770
	137.5	1390	— 4.2	460
	250	1480	— 6.9	64
	485	1580	—	—
C = 0.49 %	19.6	14.5	515	1525
	28.8	350	510	1520
	46.5	875	260	1425
	82.5	1150	167.5	1365
	136.5	1285	79.3	1230
	260	1400	0	835
	510	1525	— 13.9	360
	—	—	— 16.7	137
C = 0.84 % 1st sample a.	58.6	192	515	1230
	78.5	580	268	1070
	135	880	160	990
	254	1080	78.6	850
	505	1230	0	605
	—	—	— 33.3	370
	—	—	— 46.3	150
	—	—	— 51.7	11.3
C = 0.84 % 2d sample b.	58.1	3.7	505	1155
	74.7	442	245	1070
	137.5	860	134	965
	245	1040	75	875
	495	1155	0	670
	—	—	— 16.7	595
	—	—	— 26.7	535
	—	—	— 43.0	370
	—	—	— 48.5	260
	—	—	— 53.3	140
	—	—	— 57.6	22.1
C = 1.21 %	58.7	128	535	1200
	79.2	550	270	1080
	124	865	161.5	1015
	199	1025	78.5	890
	291	1090	0	645
	515	1200	— 14.5	555
	—	—	— 21.9	500
	—	—	— 33.3	347
	—	—	— 51.7	20
UNIEUX Carbon-steel C = 0.96 %	52	43.7	495	1175
	60.6	262	253	1075
	78.5	570	165	1010
	139	915	78.2	875
	255	1075	0	640
	495	1175	— 16.0	530
	—	—	— 32.8	292

BRAND AND KIND	ASCENDING BRANCH		DESCENDING BRANCH	
	H.	I.	H.	I.
UNIEUX Carbon-steel C = 0.96 %	—	—	— 44.0	102
	—	—	— 46.4	64.7
	—	—	— 48.7	14.0
ALLEVARD Hardened Steel W = 5.5 % C = 0.59 % a.	74.2	89	515	1240
	81.0	323	270	1160
	89.0	624	166.5	1120
	113.3	880	153.5	1115
	161.5	1050	105	1060
	183	1085	98	1055
	269	1140	55	985
	505	1240	33.3	940
	—	—	23.9	920
	—	—	0	850
	—	—	— 25.0	705
	—	—	— 44.6	545
	—	—	— 56.6	415
	—	—	— 72.7	23.7
Unhardened Steel	26.9	122.5	495	1515
	31.7	630	280	1420
	55.0	1050	164	1350
	113	1255	52.1	1180
	290	1425	0	900
	490	1510	— 16.2	630
	—	—	— 21.6	350
	—	—	— 25.8	5.8
Hardened Steel Section 0.25 cm. square b.	72.3	161	495	1230
	96.5	840	257	1160
	136.5	970	168	1110
	257	1125	0	850
	495	1130	— 39.0	670
	—	—	— 58.5	450
	—	—	— 60.5	410
	—	—	— 67.2	136.5
Nickel-steel Ni2. Ni = 3 % C = 0.7 %	58.6	153.5	455	990
	78	525	242.5	930
	121	750	137.5	860
	240	905	78.5	805
	450	980	0	640
	—	—	— 29.6	490
	—	—	— 39.0	353
	—	—	— 42.8	290
	—	—	— 47.1	199
	—	—	— 49.0	153.5
	—	—	— 53.5	10.5
Manganese-steel A. Mn = 0.7 % C = 0.46 %	34.1	139.3	460	1390
	34.5	121.5	270	1325
	43.5	700	260	1320
	52.5	870	140	1245
	99.5	1130	134.5	1230
	159	1240	80.8	1140
	264	1330	59.2	1095
	515	1390	0	860
	—	—	— 16.2	705
	—	—	— 27.3	395
Tungsten-steel V2. W = 2.7 % C = 0.76 %	70.1	28.6	510	1240
	78.2	358	269	1115
	89.0	635	157.5	1060
	113.0	855	53.8	930
	161.5	995	0	800
	291	1115	— 26.9	685
	490	1240	— 53.8	480
	—	—	— 59.3	352

was spoiled by too prolonged a heating. The ring of Boehler Boreas steel broke while being machined. Finally it was not possible to procure rings of molybdenum-steel and of very highly carburetted steel.
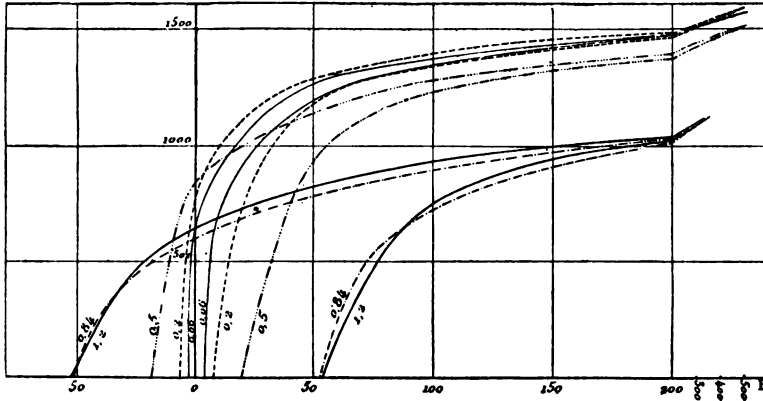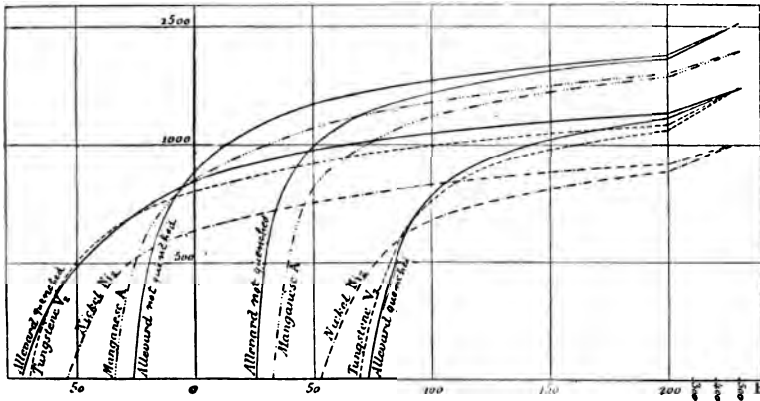

FIG. 9.

FIG. 10.

The cyclic curve of magnetization of the rings examined was constructed between field's limits of ± 500 units (Table VI). Figs. 9 and 10 show half of the cyclic curves. Fig. 9 refers to carbon-steels, the percentage being indicated on each curve; Fig. 10 refers to the other steels.

All the rings had a mean diameter of 11 cm.; most of them had a cross-section 1 cm. square; the ring *b* of Firminy steel with 0.84 per cent of carbon, the ring of nickel-steel and that of manganese-steel had circular sections 1 cm. in diameter; finally the ring *b* of Allevard steel had a section 0.5 cm. square.

The curve corresponding to the ring *b*, with 0.84 per cent of carbon, is not indicated in Fig. 9. Although its coercitive field is greater than that of sample *a*, both curves have the same appearance. The curves corresponding to the Unieux steel and to the ring *b* of Allevard steel are not represented in the diagram.

The rings were quenched at about 800° C., except in the case of the carbon-steels containing 0.06 per cent and 0.2 per cent of carbon, which were quenched respectively at abont 1000° and 850°.

TABLE VII. — *Closed Magnetic Circuits.*

	Coercitive Field	Intensity of Residual Magnetization	Intensity of Maximum Induced Magnetization	Hysteresis
C %				
Carbon-steels (Firminy) . . . . . { 0.06	3.2	625	1560	28000
0.20	7.4	770	1590	68000
0.49	19.3	835	1525	108000
a 0.84	52	605	1230	170000
b 0.84	58	670	1155	217000
1.21	53	645	1200	182000
Carbon-steel (Unieux) 0.96	50	640	1175	165000
Allevard steel, quenched, W = 5.5 % { a 0.59	73	850	1240	280000
b 0.59	70	850	1230	265000
Allevard steel, not quenched 0.59	26	900	1515	115000
Tungsten-steel (Assailly) (V₂) W = 2.7 % 0.76	69	800	1240	260000
Nickel-steel (Ni₂) Ni = 3 % 0.70	54	640	990	177000
Manganese-steel (Mn₂) Mn = 0.7 % . . 0.46	33	860	1390	142000

The principal results obtained with these rings, i.e., the most interesting points of the curve of magnetization have been tabulated in Table VII as follows:

Value of the coercitive field, i.e., the value of H when I = 0. Intensity of residual magnetization, i.e, value of I when H = 0. Intensity of induced magnetization when H = 500, i.e., the intensity of maximum magnetization ob-

tained in these experiments, in the case of each steel. The
table contains, moreover, the value of the hysteresis of each
steel, i.e., the amount of energy transformed into heat while
the steel is undergoing a complete cycle of magnetization.
This quantity is equal to $\int H d J$, and is obtained by measuring
the area of the curve of magnetization; it is expressed in ergs
per cubic centimeter of the substance examined, and refers to
a cycle between field's limits of about $\pm$ 500.

By comparing the coercitive fields obtained in the case of
rings and of bars of the same steel (Tables VII, III and IV)
it is found that this concordance is generally satisfactory.*
Some differences exist, however, but they do not occur sys-
tematically and do not appear to be caused by a difference in
the method. When the agreement is not satisfactory, pref-
erence should be given, I believe, to the determinations made
with the bars. The determinations made with rings are in
greater harmony with theoretical conditions, but, for various
reasons, the results are less reliable. The metal, for instance,
may be somewhat altered during the shaping of the ring
while hot; this, probably, happened in the case of the Fir-
miny steel with 1.2 per cent of carbon and of the Unieux steel.
Moreover, on account of the length of the preparation and
examination of the rings (hardening, dressing of the surfaces
of contact, mounting, construction of the curve), I have
studied only a single ring and a single quenching for each
kind of steel, except in the case of the Firminy sample with
0.84 per cent of carbon and of the Allevard steel, of which
two rings with different sections were examined. The testing
of bars, on the contrary, being rapid, I was able to multiply
the tests, and the results, which have thus been checked, are
more reliable.

The influence of an increasing percentage of carbon may
be followed. The coercitive field increases continuously when
the amount of carbon does not rise above 1 per cent (the study
of the bars indicates that a maximum must exist, for the
coercitive field, when the steel contains about 1.2 per cent of
carbon). The intensity of residual magnetization increases,
at first, with the amount of carbon; it reaches a maximum

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* See remarks, page 109.

when the metal contains 0.5 per cent of carbon; it then decreases with further increase of carbon. The intensity of maximum induced magnetization diminishes when the percentage of carbon increases. Finally, the *hysteresis* increases with the carbon-content. From the results obtained with bars it would seem that the *hysteresis* reaches a maximum when the amount of carbon is more than 1 per cent. It seems probable that the rings of Firminy steel with 1.2 per cent of carbon, and of Unieux steel with 0.96 per cent of carbon were somewhat altered when hot, and that the values of the coercitive field and the hysteresis, here tabulated, are too small.

With a closed circuit it would be advantageous, with regard to the magnetic flux, to use steels containing from 0.6 to 0.7 per cent of carbon, but the magnets would not be very stable. For the construction of ordinary magnets it is always advantageous to use steels more highly carburetted.

From an examination of the curves it is seen that the introduction of various metals modifies little the residual intensity of a closed circuit; it increases the coercitive field and the hysteresis, it diminishes the intensity of maximum induced magnetization.

[To be concluded in the next number of *The Metallographist.*]

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ALLOYS.[*]

By Prof. CHANDLER ROBERTS-AUSTEN, C.B., D.C.L., F.R.S.

THE belief has long been prevalent that diffusion must take place against gravity when a denser metal is placed below a column of a lighter molten metal, and the results given in the Bakerian lecture of the Royal Society for the year 1896[†] showed that such diffusion does take place in molten metals just as is the case when salts diffuse in water, the curves representing the diffusion of molten metals and

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[*] Lectures II and III of a series of Cantor lectures, delivered to the Society of Arts, March 22 and 29, 1897. Abridged. The first lecture was published in the April number of *The Metallographist.*

[†] *Phil. Trans. Royal Soc.*, Vol. CLXXXVIIA, 1897, page 383.

the diffusion of salts being of the same order. The continuation of the experiments with molten metals led to the recognition of the remarkable fact, which is probably of much industrial importance, that diffusion of metals can readily be measured not merely in molten but in *solid* metals. A history of the subject has been given in the Bakerian lecture (to which reference has just been made), and until the results of the experiments were published in that lecture, no attempt had, so far as I am aware, been made to determine in units of diffusivity, the rate of the interdiffusion of solid metals. In dealing with the history of the views as to the possibility of diffusion in solid metals, it was stated that a very interesting observation was made in 1820 by Faraday and Stodart,* who in the course of an investigation on the alloys of iron with other metals, note their failure to produce certain alloys by "cementation," but consider it "remarkable" in the case of platinum that it will unite with steel at a temperature at which the steel is not affected. This early recognition that alloys would be produced by cementation is very curious. It shows that Faraday and Stodart had observed a creeping molecular action occurring at a temperature below the fusing points of either platinum or carburized iron. They pointed out that solid steel and platinum, in the form of bundles of the mixed wires of these metals, may be welded together "with the same facility as could be done with iron or steel," and they showed that on etching the surface of the welded mass by an acid "the iron appeared to be alloyed with the platinum." Their interest in this singular fact led them to promise some direct experiments on "this apparent alloy by cementation"; but, unfortunately, their intention does not appear to have been carried into effect.

The experiment by Faraday and Stodart enables us to approach the consideration of the question of the analogy of carburized iron to ordinary saline solutions. It is necessary to bear in mind that there is abundant evidence of the penetration of iron by carbon, even in its diamond form. The diamond penetrates iron, and, moreover, the action is reciprocal, for at a temperature of 1100° the vapor of iron pene-

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* *Quarterly Journal of Science*, Vol. IX, 1820, page 319.

trates the diamond.* As yet, however, the rate at which carbon will penetrate iron at any given temperature demands investigation and measurement; some data are, however, already available. The process of cementation has been exhaustively studied by Mannesmann,† and reference will be found in the Bakerian lecture to the work of Colson.‡ As a contribution to the history of the subject the following curve (Fig. 1) taken from a paper I communicated§ to the Iron and Steel Institute in 1896, may be useful. The co-ordinates of the curve are respectively *distance* to which the carbon has penetrated a mass of iron, and the *amount* of carbon which has so penetrated. If this curve be compared with those which represent either the diffusion of common salt in water,
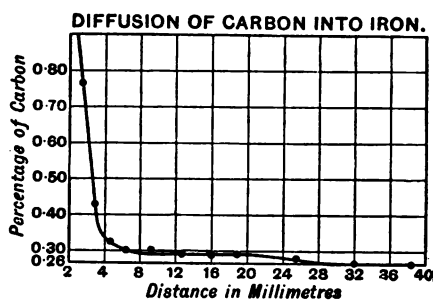
FIG. 1.

or the diffusion of gold or platinum in lead (see Bakerian lecture), it will be found that the curve for the carburization of iron is a true diffusion-curve, and this points to the *solubility* of carbon in the iron.

It will now be well to indicate the nature of the evidence afforded by the microscope as to the mode of existence of the carbon in the iron under varying conditions of thermal treatment.

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* Osmond, *Comptes Rendus,* March 16, 1891.

† *Verhandlungen des Vereins zur Beförderung des Gewerbfleisses,* 1879, Vol. LVIII, page 31.

‡ *Comptes Rendus,* Vol. XCIII, 1881, page 1074; and Vol. XCIV, 1882, page 26.

§ *Journal of the Iron and Steel Institute,* No. I, 1896.

[Prof. Roberts-Austen describes and illustrates here the microstructure of steel. This has been done exhaustively elsewhere in *The Metallographist.* The reader is especially referred to page 30 et seq., to the illustrations of Mr. Osmond, accompanying his paper on "Metallography considered as a Testing Method," and to page 210 et seq. — ED.]

It will therefore, I trust, be evident that photomicrography affords most precious information both as to the constitution of steel and as to the complication of relations which may subsist between carbon and iron.

In order to make any discussion of these relations possible, it is necessary to bear in mind the dominant fact so beautifully developed by Mr. Osmond that, as carburized iron cools down from a high temperature, there are several points of arrest in the cooling which mark important and critical changes. In round numbers there is one such point at 850° C. called by Mr. Osmond Ar_3; there is another at 750° C. called Ar_2; and yet another at 650° C. called Ar_1. The changes which occur respectively at 850° C. and 750° C. can, as I showed some years ago, also be detected in the purest iron yet produced, and this fact has recently been confirmed by Messrs. Hicks and O'Shea.* It is claimed, therefore, that these points represent allotropic changes in the iron, a view which receives strong support from the fact that the magnetic properties of iron change distinctly and more or less sharply at 750° C. (Ar_2).

Let it be assumed, as has already been suggested above, that the diffusion of carbon in iron is analogous to the diffusion of common salt in water. The iron or "ferrite" corresponds to the water, but the diffusing chloride of sodium is not represented by carbon, but by a compound of carbon and iron, Fe_3C, the existence of which, in steel, can be abundantly demonstrated, and to this compound the name "cementite" is given. If a hot solution of common salt were allowed to cool, salt would fall out of solution, and in the same way if a hot solution of cementite, Fe_3C, in iron be allowed to cool, Fe_3C will fall out of solution, and, in highly carburized steels, segregated or free cementite will "fall out," just as the salt

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* Commemoration Volume, University College, Sheffield, 1897, page 52.

did from the water. Turn to Fig. 7, page 21 (*The Metallogra-phist*),* and it will be seen that it contains carburized kernels of pearlyte; it is a variety of steel low in carbon, there is only sufficient dissolved carbide, Fe_3C, to separate out in patches as the mass cools. In steel with more carbon, such as is shown in Fig. 9, facing page 1, the carbide separates out and pervades one part of the mass as pearlyte, together in another part of the mass with some segregated " cementite" which constitutes a broad band across the specimen.

What then is "martensite"? According to Mr. Osmond, it appears to be formed during the heating of a mass of carburized iron by a true internal "cementation" of the " ferrite " or free iron of the mass, an operation which takes time and is proportionately longer the lower the temperature is. If a mass of carburized iron (within the range of car-burization, that is, which constitutes steel) be rapidly cooled from a high temperature by quenching, the carbon remains in the form of martensite, as in Fig. 10, page 23, and the steel is " hard." If the cooling is rapidly effected by quench-ing small samples of steel in water mixed with ice, the cooled metal should reveal a structure which nearly approaches that possessed by the metal while it is hot; and Mr. Osmond has shown that the proportion of segregated cementite varies with the temperature of quenching. If this temperature exceeds 1000° C., a percentage of dissolved carbon amounting to 1.60 per cent may be reached without the isolation of cementite. At this stage a new constituent appears — the one Mr. Os-mond has been so good as to connect with my name; and the most salient of the properties of "austenite," so far as it is possible to ascertain them, is that of being scratched by a darning-needle or by apatite. It is a mixture with properties closely resembling those of steel with 12–13 per cent of man-ganese and steel with 25 per cent of nickel. When, however, the percentage of carbon exceeds 1.6 per cent, cementite re-appears.

It will now be possible to trace the relation between the freezing-point curve of the carbon-iron series and that of

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* The photographs of Mr. Osmond, used to illustrate these lectures, have been reproduced elsewhere in *The Metallographist*, as indicated by the references given. — ED.

certain alloys. Usually when two substances which form neither definite compounds nor isomorphous mixtures are soluble in each other, it is known that their curves of fusibility or of solubility, for they are practically the same thing, in most cases is composed of two branches; one of these branches corresponds to the deposition in a solid state of one of the constituent substances of the mass; the other branch corresponds to a deposit of the second substance. Let me remind you of the case of the lead-tin series (see Fig. 5 of last lecture) which belongs to the class of simple solutions. At a temperature near the melting-point of lead an alloy of lead and tin containing 50 per cent of each metal would be entirely fluid, and the two metals would be in mutual solution. If the alloy were to cool down to 220°, solid lead would begin to crystallize out; the solid lead, the analogue of ice in a saline solution, can exist in contact with the fluid so long as the temperature is kept constant. As the temperature falls, more and more lead crystallizes out until at 180° the residue, which by this time contains nearly 70 per cent of tin, solidifies as a whole, and this alloy is the *eutectic* alloy. In the curve, Fig. 2, there are the two branches, AB, BD, and the eutectic, *ac*. In order to obtain this curve I prepared a series of carburized irons as free as was convenient to make them from silicon and manganese, and have taken freezing-point curves of them by the autographic recorder, precisely as if it were merely a question of the solidification of an ordinary series of metallic alloys. Thus the iron containing, say, 3 per cent of carbon was found to have three freezing-points, which occurred respectively at 1200°, 1120° and 680.° Putting all the results for the entire series of carburized irons in a curve and adding some results obtained by Mr. Osmond (for he has been engaged in the investigation of the subject since 1888),* the appended diagram, Fig. 2, will be the result.† It should be

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* *Ann. des Mines,* Vol. XIV, 1888, pages 39 and 59.

† To avoid any possible confusion resulting from a comparison of this diagram with that shown on page 220, it is perhaps well to recall that the latter indicates only those evolutions of heat accompanied by structural changes which take place in the cooling metal long after it has entirely solidified. In other words, it corresponds to the branches in the left-hand corner of Prof. Roberts-Austen's diagram. The branches ME

remembered that points in the same vertical line represent points of arrest in the cooling of a single carbon-iron alloy.

I should add that my assistant, Mr. Stansfield,* in a discussion of a paper read at the Institution of Civil Engineers in 1895, pointed to the analogy of certain members of the carburized-iron series to cryohydrates, and Guthrie showed that the cryohydrates of salts are analogous to alloys.

The line AB represents iron containing dissolved carbon and the line BD indicates that free carbon in the graphitic form separated out. The line aBc should therefore correspond to a eutectic of liquid iron and carbon. As Fe_3C dis-

CARBURIZED IRON FREEZING-POINT CURVES.

Carbon per Cent
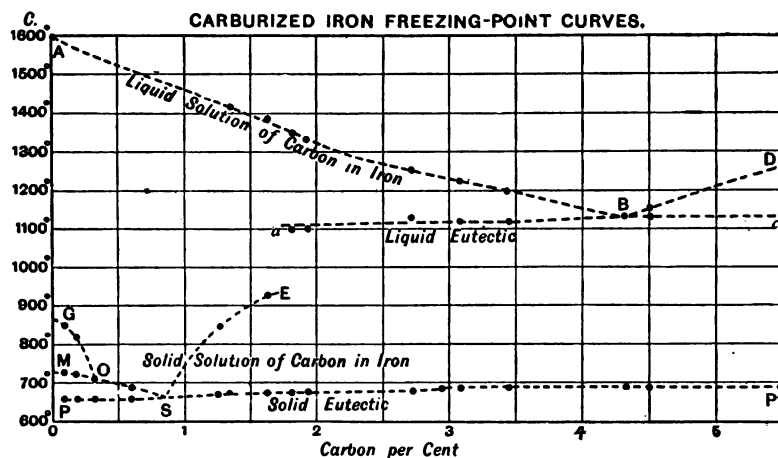
FIG. 2.

sociates at a temperature of 1100°, it can only exist under the osmotic pressure of dissolved carbon, and, therefore, cannot separate out above the line ac, but must be formed at or below this temperature in the cooling mass of iron.

What then is the line PP'? It is clearly the eutectic of a solid solution.

What then is hardened steel? According to Mr. H. Le Chatelier,† it is a solution of a carbide of iron, Fe_3C, and of a

and NE of the diagram on page 220 correspond respectively to the branches GOS and ES of this diagram, while for reasons stated on page 221 (foot-note) the branch MO was not indicated. — ED.

* *Proc. Inst. Civil Eng.*, Vol. CXXIII, 1895, page 260.

† *Revue Générale des Sciences*, January, 1897, page 22.

variety of iron. This solution is like the glasses in a state of supersaturation or surfusion, but, unlike the glasses, quenched (hardened) steel is not amorphous but crystalline, and its structure resembles that of the isomorphous crystalline mixtures. It is this possibility of the existence of solid solutions that we are now confronted with, and the experiments on the diffusion of solid metals derive much interest from the light they throw on the theory of the hardening of steel.

It will be seen that there are branches in the left-hand corner of the diagram which remain to be explained. There is a branch, GO, which begins in carbonless iron at 860° (Ar_3). It corresponds to the beginning of the aggregation of the ferrite, that is, of the iron itself in the solid mass. It must be, and is, according to the theory I have so long advocated, a true allotropic change; it is the change of γ iron into the β form in steels which are not saturated with Fe_3C. It will be seen that there is a point corresponding to about 0.9 per cent of carbon; this, according to Mr. Osmond, is the point at which a iron and the carbide Fe_3C are simultaneously deposited at a constant temperature. It is the point at which γ iron and Fe_3C are mutually saturated, and at this point the phenomena which occur are exactly comparable with the solidification of eutectic alloys. The line PP′ then represents the change at 650° of iron containing about 0.9 per cent of carbon, from a solid solution (martensite) to a mechanical mixture of ferrite and cementite, known as pearlyte. This occurs through all the range of carburized irons, from the mild steels to the cast irons. To the right of the point S, as carburized iron cools down, cementite separates out, and about 0.9 per cent of carbon still remains in solid solution in iron. It must be remembered that it is soluble in one of the allotropic modifications of solid iron. At 650° the iron, during slow cooling, undergoes allotropic modification, and is converted into a form of solid iron which will not dissolve cementite.

There is, however, one other point of analogy between carburized iron and saline solutions, and it is as follows. When Eggertz's test is applied to steel it is well known that a certain portion of the carbon known to be present in the steel is not indicated by the test; it is, in fact, known as " missing

carbon," and it is reasonable to conclude that the carbide, Fe_3C, when dissolved, that is to say as martensite, becomes in part dissociated into its " ions," which remain free together with molecules which are intact.[*]

From this Mr. Osmond concludes that the fraction of carbon exists as Fe_3C, in solution, and in annealed steels it forms the constituent called sorbite.

The line MO appears to be another solid eutectic; it corresponds to the 750° Ar_2 change in the iron, and requires further investigation.

The fact that there is solution of carbon in iron is therefore clearly demonstrated, and the question arises, may it not, under certain conditions, be released from solution in the diamond form and not in the graphitic? Moissan[†] has enabled us to answer this question, and has shown that diamonds may be readily produced. Carburized iron expands on solidification, and a mass of fused iron will become solid at its surface and will contract; but when, in turn, the still fluid mass in the interior cools, it expands against the solid crust and consequently solidifies under great pressure. Dissolve such a mass of carburized iron in nitric acid to which potassic chlorate has been added: treat the residue with caustic potash, submit it to the prolonged attack of hydrofluoric acid, then to boiling sulphuric acid, and finally fuse it with potash to remove any traces of carbide of silicon, and carbon is left — but in the form of diamonds.

It will, I trust, be evident from the foregoing remarks that there is the closest analogy between the carburized iron and ordinary metallic alloys, and that complicated movements may take place in solids.

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[*] Hogg, *Journal of Iron and Steel Institute*, 1896, Part II.
[†] *Comptes Rendus*, Vol. CXVIII, 1894, page 324.

ALLOTROPIC IRON AND CARBON,*

WITH A FEW NOTES ON THE EFFECT OF SULPHUR, PHOSPHORUS AND MANGANESE.

By ERNEST HENRY SANITER.

THE controversy as to the cause of the glass-hardness of quenched carbon-steel still remains undetermined. It is with the hope of assisting towards its determination that I bring my further work before you — work which I hope may be recognized as an honest endeavor to arrive at the truth, and not as special pleading in favor of one or other of the contending hypotheses.

The results here given are a continuation and amplification of those obtained by the hot-etching process as set forth in my paper on carbon and iron. For the sake of convenience I have divided the paper into three sections as follows :

Section I. The structure of pure carbonless iron at a bright red heat.

Section II. The structure of pure carbon-iron compounds at a bright red heat.

Section III. The effect of moderate quantities of sulphur, phosphorus and manganese on the structure of carbonless iron at a bright red heat.

The principle followed in selecting the specimens for this investigation was that of using material entirely free from the effect of mechanical treatment — in other words, specimens in which the normal structure would be as perfect as possible.

This object has been attained, either by using metal slowly cooled from the molten state, or by thorough annealing of the specimens which had received mechanical treatment.

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* Iron and Steel Institute, May meeting, 1898.

Section I. — The Structure of Pure Carbonless Iron at a Red Heat.

The method of etching was that described in my last paper, except that it was found that by extending the time of etching from fifteen to twenty-five seconds the structure was better developed.

Photomicrographs Nos. 1 and 2 (A, B, C, D, E)* are etchings of pure carbonless iron, to which I will now draw attention in detail.

No. 1† is pure normal iron, and shows the cubic structure very well.

No. 1. Pure Carbonless Iron.
C trace; S 0.018; P 0.01; Mn 0.23.
Magnified 250 diameters.
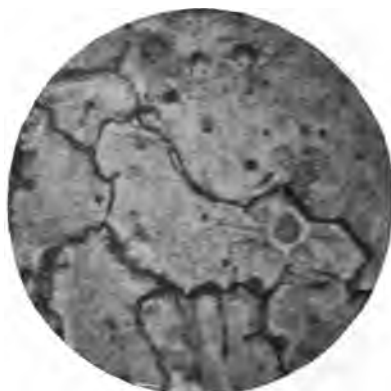
No. 2 A. Pure Carbonless Iron.
C trace; S 0.015; P 0.005; Mn 0.10.
Magnified 250 diameters.

No. 2 (A, B, C, D, E)* are all from different parts of one piece of pure iron etched at a bright red heat,‡ and show

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* Photomicrographs No. 2 (B, C, D and E 1) have not been reproduced here. They present very nearly the same characteristics as No. 2 A. — ED.

† Mr. Stead was good enough to instruct me how to develop the cubic structure in pure iron.

‡ The temperature of the hot etching was judged by the eye, but was afterwards carefully checked by the Le Chatelier pyrometer, which showed it to be about 900° C. Owing to the necessary shaking of the crucible during etching, it is not convenient to use the thermo-couple during the actual operation. Mr. Stead was good enough to take the temperature with his instrument.

the crystalline structure very well. The dark irregular lines on all the hot-etched series are the granular junctions.

The dark spots are due either to imperfections in the specimen or irregularity of etching caused by gas exuding from the metal.

(A.) In the lower portion of the large central grain will be seen an almost perfect rhomboid.

(B.)* In the center of the large central grain is an almost perfect triangle showing a laminated structure. It will be observed, however, that the left-hand side of the triangle is a straight line only in part, the lower portion being indefinite and irregular; the triangle is, therefore, probably accidentally caused by the interference of another crystal.

(C.)* The somewhat irregular figure in the central grain shows a very well-developed laminated structure, and although there are several definite angles, they are none of them right angles.

(D.)* This shows a figure with a well-defined angle, which might be a portion of a rhomboid; the laminated structure is present.

(E 1* and 2.) This shows a well-defined laminated structure, and several well-defined acute angles. Particular attention is drawn to the central line, which is evidently the edge of a plate, and the figure on the right-hand side. The latter is enlarged to 1000 diameters in E 2, which shows very clearly the laminated structure.

The acute angles of the above figures vary between 52° and 67°; this variation, no doubt, being due to the angle made by the true facet of the crystal with the surface of the specimen.

Now, as is well known, the angles of the crystals of normal iron are right angles, as illustrated by Photomicrograph No. 1, while the angles of those developed by etching at a bright red heat are none of them right angles.

This shows that iron at a bright red heat changes its crystalline form, and is therefore dimorphous.

The fact that iron is dimorphous, together with the evidence brought forward by Osmond and others, appears to

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* Photomicrographs No. 2 (B, C, D and E 1) have not been reproduced here. They present very nearly the same characteristics as No. 2 A. — ED.

my mind sufficient to establish the existence of an allotropic modification.

It yet, however, remains to be demonstrated whether allotropic iron is hard or soft.

Owing to my very slight knowledge of crystallography, it is only with very great diffidence that I venture to express an opinion as to the crystalline form assumed by allotropic iron ; and I venture to hope that some competent authority will give us the benefit of his experience.

I think the figure on No. 2 A indicates a rhombohedron, and that the figures on B, C, D and E point in the same direction.

No. 2 E (2).   Pure Carbonless Iron.
Magnified 1000 diameters.
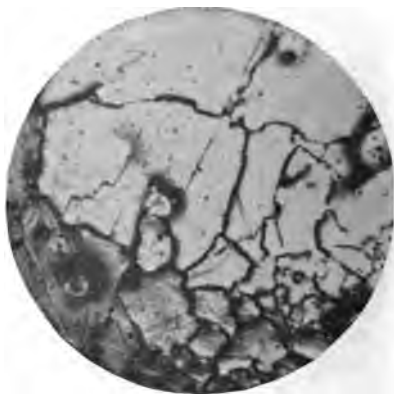
No. 3.   Pure Carbon-steel.
C 0.10 ; S 0.021 ; P 0.014 ; Mn 0.20.
Magnified 250 diameters.

In connection with this it is interesting to remember that Mr. Osmond considers that the triangular figures of martensite represent the octahedral crystallization of gamma-iron. The rhombohedron is a hemihedral form of the hexagonal system.

Section II. — The Structure of Pure Carbon-iron Compounds at a Bright Red Heat.

Photomicrographs 3, 4 and 5 were etched at a bright red heat.   The general explanation given in Section I, with reference to defects and granular junctions, applies equally to these.

Photomicrograph No. 3 (0.1 per cent carbon). — The portion containing the carbon is indicated by the reduced size of the grains, the carbon, in diffusing through the metal on heating, breaking up the large grains.

It is noticeable that in the large grains are distinct indications of the allotropic structure, particularly in the grains left and right of the center.

At the same time there are not wanting similar indications in the smaller grains where the carbon is present.

No. 4 (carbon, 0.185 per cent). — Here the small grains containing carbon largely predominate, but as far as this
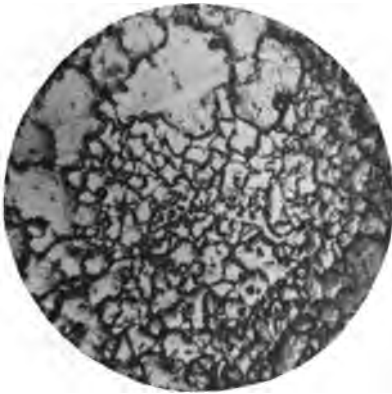
No. 4.   Pure Carbon-steel.
C 0.185; S 0.018; P 0.010; Mn 0.23.
Magnified 250 diameters.

No. 5.   Pure Carbon-steel.
C 1.0; S 0.014; P. 0.008; Mn 0.16.
Magnified 250 diameters.

method indicates, they are amorphous.   In the few large grains to the left, which, it is believed, contain little or no carbon, there are again indications of the allotropic structure.

A word of explanation is necessary as to the existence of these large grains.   In cast steel, slowly cooled, the carbide areas are large and few, and therefore probably have not time or cannot diffuse through the whole mass in the same manner as worked steel with its large number of small carbide areas.

Photomicrograph No. 5 (carbon, 1 per cent) shows the acicular crystalline structure of high-carbon steel, as given in my previous paper.

Section III. — The Effect of Moderate Quantities of Sulphur Phosphorus and Manganese on the Structure of Carbonless Iron at a Bright Red Heat.

Photomicrograph No. 6 (annealed wrought iron; phosphorus, 0.06 per cent). — It will be noticed that the fibrous structure has entirely disappeared during annealing. The allotropic structure is clearly defined, but there are dark markings on the right-hand side of the central grain peculiar to this specimen. The laminated appearance is absent.

Photomicrograph No. 7 (sulphur, 0.064 per cent; manganese, 0.50 per cent). — In this case the structure is splendidly defined, but shows several modifications from that of pure iron; for although the right-hand crystal shows no right angles, the left-hand one does, while the laminations are of a different character to those shown by pure iron.

These results seem to indicate that small quantities of other elements besides carbon modify the allotropic structure.

Conclusion.

The calcium-chloride hot-etching method develops on pure iron and carbon steel three distinct structures (compare Photomicrographs Nos. 2, 4 and 5), two of which may exist together in the same steel.

These three structures may be named for convenience as follows :

(1) "The allotropic structure," found in pure carbonless iron.

(2) " The amorphous structure," found in steel of medium carbon.

(3) "The acicular structure," found in high-carbon steel.

The allotropic and amorphous structures are found side by side in iron containing 0.1 and 0.18 per cent of carbon. (See Photomicrographs 3 and 4.)

The amorphous and acicular structure are found together in iron containing 0.60 per cent carbon. *

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* *Journal of the Iron and Steel Institute*, 1897, No. II, page 128, Plate V.

I have already discussed the allotropic and acicular structures, but with regard to the amorphous structure I feel quite undecided.

Is it that carbon between 0.1 and 0.43 per cent forms an amorphous compound with iron, or is it that there is a fight between the acicular and the allotropic structures, which ends in the breaking down of both, and the consequent formation of an amorphous mass?

It is important, in view of the deductions that may be drawn from these results, to compare the microscopic observations with the cooling curves of pure iron and carbon steel.
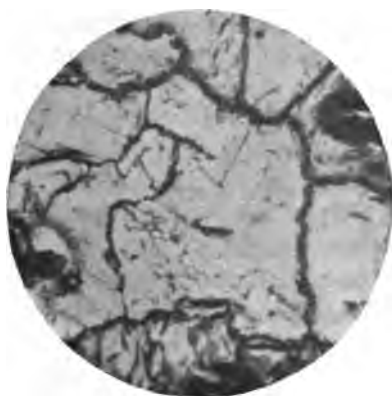
No. 6. Annealed Wrought Iron.
C trace; S 0.003; P 0.06; Mn 0.17.
Magnified 250 diameters.

No. 7. Carbonless Iron.
C trace; S 0.064; P 0.02; Mn 0.50.
Magnified 250 diameters.

From the cooling curves of iron and steel,† it is seen that pure electrolytic iron shows only one arrest, viz., at 870,‡ which·is considered to be caused by the allotropic change. (Compare with Photomicrographs No. 2.)

The low-carbon steel (carbon not stated) gives two arrests, first the allotropic change, commencing at 750°, and second the carbon change, commencing at 665°. It is to be noted that the allotropic arrest occurs at a lower temperature, and that quantitatively it is only about one-fourth of that on

† See Prof. Roberts-Austen's "Introduction to the Study of Metallurgy," 1898, page 156.

‡ The arrest is so slight at 750° as to be barely noticeable.

pure iron. (Compare Photomicrograph No. 4, 0.18 per cent
of carbon.)

High-carbon steel (carbon, 1.25 per cent); here again we
have only one arrest of temperature, said to be the allotropic
and carbon changes combined, and commencing at 675°. It
is to be noted that its duration is abnormally long, showing
the great evolution of heat caused by the carbon change, and
that it commences at the same temperature, as far as can be
judged from the diagram, as the carbon change in the low-
carbon steel. (Compare Photomicrograph No. 5, 1 per cent
carbon.)

Now the decrease in the duration of the arrest caused by
the allotropic change with increasing carbon seems to me
very important, in view of the microscopic results here pre-
sented.

It would naturally be expected from the microscopic
structure, that with iron with no carbon the allotropic change
would be at its maximum, as shown by the heating curve.

In 0.18 per cent of carbon steel (Photomicrograph No. 4),
which shows little allotropic iron, one would naturally expect
the allotropic arrest of temperature proportionately less, as
is shown to be the case by the cooling curve of low-carbon
steel.

Then Photomicrograph No. 5 shows no allotropic iron,
and at the same time the cooling curve shows only one arrest,
namely, that which commences at the carbon-change tem-
perature.

The fact of a gradual reduction of the duration of the
arrest, due to the allotropic change, with increasing carbon,
and its final disappearance as a separate point, taken together
with the microscopic evidence of the structure at a red heat,
seems to show that the allotropic arrest disappears, because
there is no longer any allotropic iron, and further, that car-
bon is actually inimical to the presence of allotropic iron.

Under these circumstances there would only remain the
carbide theory to account for the hardness of quenched steel.

THE HARDENING POWER OF LOW-CARBON STEEL.

By HENRY M. HOWE.

THE allotropic theory of the hardening of steel may, like so many other important theories, have to be accepted or rejected not on direct proof or disproof, but on the accumulation of circumstantial evidence for or against it. The rival explanations of hardening are carbon-condition and stress. A promising line of inquiry has seemed to me to study the hardening power of low-carbon steel, or in other words, to ask whether by any *tour de force* the specific effects of hardening can be induced either in iron free from carbon, or in almost carbonless iron, to a degree too great to be explained by the small quantity of carbon present. Prominent among these specific effects are increase of tenacity and of mineralogical hardness, i.e., of the resistance to scratching, etc., elevation of the elastic limit, and decrease of ductility. I have already offered a large number of cases in which some of these specific effects have been caused to a degree too great to be explained readily by the quantity of carbon present, e.g., when steel containing only 0.022 per cent of carbon, no manganese, and a trace of silicon, had its tenacity raised about 48 per cent by sudden cooling and its elastic limit raised about 86 per cent, and when Mr. Hadfield's wrought-iron containing 0.02 per cent of carbon had its elastic limit thus raised by 81 per cent.

When Mr. C. A. Tripler installed machinery for making liquid air in quantity, an opportunity came for testing this question more thoroughly by using a much more sudden cooling than could be had with the freezing mixtures which I had previously used. He generously supplied me with several gallons of liquid air, and with this I froze a considerable bath of mercury, and one of alcohol. In the melting mercury and in the melting alcohol I was then able to quench hot wires of steel almost free from carbon, and also for comparison, like wires of platinum and of copper.

My examination of the wires thus treated has been interrupted when but a few of them have been tested, but, as the

interruption will be a long one, I think it best to publish at once the results thus far reached, which I condense in the following tables :

TABLE I. — *Percentage Gain of Tenacity and Elastic Limit and Percentage Loss of Elongation on Quenching Low-carbon Steel in Melting Mercury.*

Series	Percentage Increase in		Percentage Decrease in Elongation
	Elastic Limit	Tenacity	
29	Gain 157 per cent	Gain 54 per cent	Gain 95 per cent
59	Gain 17 per cent	Gain 15 per cent	Gain 6 per cent

The two steels treated had the following composition :

	Carbon	Silicon	Manganese	Phosphorus	Sulphur	Copper
Series 29 . .	0.022	traces	0	0.007	0.014	0.10
Series 59* . .	0.009	—	—	—	—	—

The carbon of each was determined by combustion by Messrs. Booth, Garrett & Blair.   Lest it be thought that the metal may have absorbed carbon subsequent to analysis and prior to these tests, let me say that the carbon determination in case of Series 29 was made on a quenched bar previously reported, the tensile strength of which was approximately like that of the quenched wire of Series 29 here given in Table II, the drillings being taken from the bar *after* the tensile test.   In like manner, the carbon here returned by Booth, Garrett & Blair for Series 59 was determined in the fragments resulting from the test of wire No. 4 which in Table I has a fibre stress of 59,100 pounds per square inch at the elastic limit, and of 110,000 pounds per square inch at the maximum load.   These fragments for analysis were taken and analyzed after the transverse tests had been made.

Series 29 is basic open-hearth steel, made by Mr. H. H. Campbell of the Pennsylvania Steel Company.   Series 59 is electrolytic iron kindly given me by the distinguished electric-heating engineer, Mr. W. S. Hadaway, Jr.

Discussion.—Reserving full discussion till the rest of the wires have been tested, we may note the considerable increase

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* The results of a complete analysis of this sample will be published shortly. — ED.

TABLE II. — *Tensile Properties of Low-carbon Steel Wires, Quenched and Annealed.*

Designation	Carbon by Combustion	Treatment	Diam.	Area of Section in sq. in.	Elastic Limit in lbs.	Maximum Load in lbs.	Elongation in inches	Elastic Limit per sq. in. in lbs.	Tensile Strength per sq. in. in lbs.	Elongation % of gauged length	Remarks
Series 29	.022	Annealed	.0203	.00032	9	15	in 2.96" .33	28,125	46,875	11.15	Broke ¾" from grip
do.	.022	Quenched in Mercury	.0214	.00036	—	26	in 3.04" .022	72,222	72,222	.7	,, 1 1/16" ,,
Series 59	.009	Annealed	.0534	.00224	60	105	in 2.57" .29	26,785	46,875	11.28	,, ⅝" ,,
do.	.009	Quenched in Mercury	.0714	.0040	125	215	in 2.92" .35	31,250	53,750	11.99	,, 1" ,,

of tenacity and elevation of the tensile elastic limit caused by quenching ; that quenching in melting mercury is much more energetic than quenching in the very much colder but lighter melting alcohol ; and that the elevation of the transverse strength and elastic limit is greater than that in the corresponding tensile properties.

Should the remaining tests confirm this greater increase of the transverse than of the tensile strength and elastic limit, the question would arise whether this was due to the fact that the outer layers of the wire, which of course are cooled faster than the inner ones, play a greater part in determining the transverse strength of the whole than in determining the tensile strength.

The hardness determinations, made by measuring with a microscopic micrometer the width of many scratches made by means of a Turner sclerometer, are hardly abundant enough to be discussed with advantage, save to say that the quenched steel is decidedly harder than the annealed.

The data regarding ductility are far too scanty for discussion.

To sum this up, we find that three of the specific effects of hardening, viz., increase of

TABLE III. — *Influence of Sudden Cooling on the Transvers*

METAL	Laboratory No. of Wire	Treatment	Diam.	Span	Transverse Load, At Elastic Limit Annealed	Quenched A
			Inches	Inches		
Series 29 Steel containing 0.022 per cent of Carbon	Series 29	Annealed	.0176	1	60	—
	do.	do.	.0176	1	80	—
	Average.......	......	......	......	....	....
	Series 29 No. 8	{ Quenched in Alcohol }	.0184	1	—	100
	do.	do.	.0184	1	—	100
	Series 29 No. 3	{ Quenched in Mercury }	.0199	1	—	150
	do.	do.	.0199	1	—	?
	Series 29 No. 7	do.	.0187	1	—	80
	do.	do.	.0187	1	—	110
	Series 29	Cold Drawn	.0201	1	—	280
	do.	do.	.0201	1	—	265
Series 59 Electrolytic Iron containing 0.009 per cent of Carbon	Series 59 No. 7	Annealed	.0508	3	?	—
	do.	do.	.0508	3	180	—
	Average.......	....	......	......	....	....
	Series 59 No. 5	{ Quenched in Alcohol }	.0684	3	—	1150
	do.	do.	.0684	3	—	1030
	Series 59 No. 4	{ Quenched in Mercury }	.0664	3	—	1030
	do.	do.	.0664	3	—	1030
Platinum	—	Annealed	.0166	1	25	—
	—	do.	.0166	1	22	—
	Average.......	......	......	......	....	....
	2	{ Quenched in Mercury }	.0172	1	—	25
	2	do.	.0172	1	—	25

A. The samples of "cold drawn, Series 29," are inser

Elastic Limit and Ultimate Strength of Iron and Platinum.

Grammes		Fibre Stress, Pounds per Square Inch					
Maximum Load		At Elastic Limit			Maximum		
Annealed	Quenched A	Annealed	Quenched A	Percentage of Excess over the Annealed State	Annealed	Quenched A	Percentage of Increase on Quenching
90	—	61,800	—	—	92,700	—	—
95	—	82,400	—	—	97,800	—	—
....	....	72,100	....	....	95,250	—	—
—	120	—	90,300	25	—	108,400	14
—	110	—	90,300	25	—	99,300	4
—	270	—	106,700	48	—	192,100	102
—	250	—	?	—	—	177,800	87
—	180	—	68,900	—4	—	155,000	63
—	230	—	94,700	32	—	198,000	108
—	320	—	192,800	167	—	220,400	131
—	339	—	182,500	153	—	233,400	145
430	—	?	—	—	55,100	—	—
430	—	23,000	—	—	55,100	—	—
....	....	23,000	....	....	55,100	—	—
—	1230	—	60,500	163	—	64,700	17
—	1130	—	54,200	135	—	59,500	8
—	1900	—	59,200	157	—	109,200	98
—	1930	—	59,200	157	—	110,900	101
35	—	30,600	—	—	42,700	—	—
33	—	27,000	—	—	40,500	—	—
....	....	28,800	....	....	41,600	—	—
—	40	—	28,000	—3	—	44,800	8
—	35	—	28,000	—3	—	39,200	—6

in this column for convenience, although not quenched.

tenacity and mineralogical hardness, and elevation of the elastic limit, are induced in these specimens of iron, and two of them to a degree to my mind out of proportion to the probable effects of the minute quantity of carbon present.

In view of these results and those previously published, there can, in my opinion, hardly be a reasonable doubt that in the hardening of almost carbonless iron some agent other than carbon-condition is at work. It seems to me something to have this much definitely established.

But this only opens another question before us. Cold working, by wire-drawing and like operations, increases the tenacity greatly, the mineralogical hardness slightly, raises the elastic limit very greatly, lessens the ductility, lowers the density — in a word, induces results like those of hardening proper. Cold working consists essentially in permanent distortion or set in the cold. Like results are induced by like distortion even if the temperature at which it occurs be far above the common, perhaps even if it be as high as 632° C. ; the differences in the rates of cooling of different layers of a quenched bar should induce like interstratal distortion ; may not this distortion be the cause of the results which this paper records? Stress too has been invoked as a cause of hardening ; may not it explain my results? If so, we should find like results induced in other metals by like treatment.

·I have selected copper and platinum for comparison. Platinum should, in sudden cooling, be affected by distortion and stress like iron, because of its low thermal conductivity ; but, so far as the present results go, its transverse properties are not considerably affected by the violent cooling. A few results indicate that the mineralogical hardness of platinum is raised slightly by quenching, but the difference is within the limits of observational error. As this point is a vital one, I shall seek much fuller information concerning it.

It has been well said that the inequality in the rate of cooling and the resultant interstratal motion and distortion ought to be especially great in iron, because of the marked change in the coefficient of dilatation at the critical points where gamma changes to beta and beta to normal iron. This is equivalent to saying that allotropy ought to contribute to the hardening of low-carbon steel, though not by the retention

of allotropic iron but by its departure. I hope that my later results may throw more light on this question.

Let us examine the metals which, in view of their thermal conductivity, coefficient of dilatation, etc., ought, in sudden cooling, to undergo interstratal motion and distortion comparable with that which iron should undergo. Let us see whether these metals are affected by twisting, pulling, etc., in the cold and at moderate temperatures as much or anything like as much as iron. Let us then see whether this very rapid cooling can induce in them the effects which cold working does, and apply this knowledge to the hardening of nearly carbonless iron.

Microscopic Observation on Deterioration in Steel Rails. — Mr. THOMAS ANDREWS continues the publication of his researches dealing with the deterioration in steel rails, as revealed by the microscope. *Engineering*, April 15, page 451, and May 20, page 617.

Bibliography of the Metallography of Iron and Steel. — The four following papers should be added to Mr. Colby's bibliography published in the April number of *The Metallographist* (Vol. I, page 168). They have been numbered so as to readily indicate their proper chronological position.

126*a*. SAUVEUR, A., and HOWE, H. M. — Relation between temperature and grain of steel. — Eng. and Min. J., vol. lx, p. 537.

183*a*. RICE, F. S. — Microstructural characteristic of steel. — Trans. Amer. Microscopical Soc., Aug. 1897.

183*b*. MOLDENKE, R. — The microscope in the study of iron. — Iron Trade Review, Oct. 28, 1897, p. 19.

187*a*. KREUZPOINTNER, P. — Steel as viewed by the engineer. — Digest of Physical Tests, vol. iii, p. 22, Jan. 1898.

CORRESPONDENCE.

Magnetic Transformation and Hardening of Steel.

To the Editor of *The Metallographist.*

Sir : — In your last number (April, 1898) you review the interesting memoir of Mrs. Sklodowska-Curie on the magnetic properties of hardened steels.* On that occasion you invite discussion upon the relations which may exist between the magnetic transformation of iron and that transformation which is the cause of hardening, and you ask whether there exists, between these two phenomena, a real identity or a mere coincidence.

To make the matter clearer, I quote the whole of that passage of your article to which I just alluded.

You express yourself as follows :

"On page 117, the authoress says, speaking of the temperature of magnetic transformation : 'This temperature is precisely that which must be passed in order to harden a bar'; and on page 121 : 'In order to be hardened, steel must be quenched at a high temperature while it is in a feebly magnetic condition.'

"It would seem at first sight that the steel must indeed be in its non-magnetic condition in order to be hardened through sudden cooling, but is it, in reality, a necessary condition?

"Let us take a piece of steel containing 0.30 per cent of carbon, and let us heat it to a high temperature and then cool it past the point A_2, quenching it, however, before the point A_1 has been reached, i.e. between A_2 and A_1. It will be hardened most decidedly,† although it was magnetic at the time of quenching, since the transformation A_2, which restores the magnetic properties, had taken place.

"In the case of steel containing less than some 0.45 per cent of carbon, there exists, it would seem, a narrow range of temperature, in which the steel, although being magnetic, possesses also considerable hardening power. This range of temperature, being comparatively very narrow, may easily escape detection.

"The statement of the authoress infers that steel gains its hardening power during the retardation A_2, i.e., during the magnetic transformation, while numerous previous investigations have established quite conclusively that it is during A_1 (or $A_{3\ 2}$, as the case may be) that it acquires most, if not all, of that power.

"With over 0.45 per cent of carbon in the steel, and, therefore, for all grades of steel used in the construction of permanent magnets and for nearly all steels whose hardening power is utilized, the retardations A_1 and A_2, i.e., the magnetic transformation and that transformation which confers most of the hardening power, *occur at the same temperature,* but it does not follow that both transformations cannot take place independently. Indeed, from the evidences offered by the behavior of softer steels we are naturally led to infer that they are independent of each other, that *the steel must not necessarily be in a non-magnetic condition in order to*

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* page 107 et seq. — ED.

† "While some additional hardening power is gained during the upper retardations A_3 and A_2, as was conclusively shown by Mr. Howe and others, a very great portion of the hardening power is acquired during A_1."

be hardened by sudden cooling; that if, in the great majority of cases, it is in a non-magnetic condition when endowed with hardening power, it is a mere coincidence due to the fact that, in such cases, both transformations take place at the same temperature."

I answer to these remarks:

(1) *The magnetic transformation is not localized at the points which I have called Ar_2 or $Ar_{3\,2}$ in steels which have several critical points.*
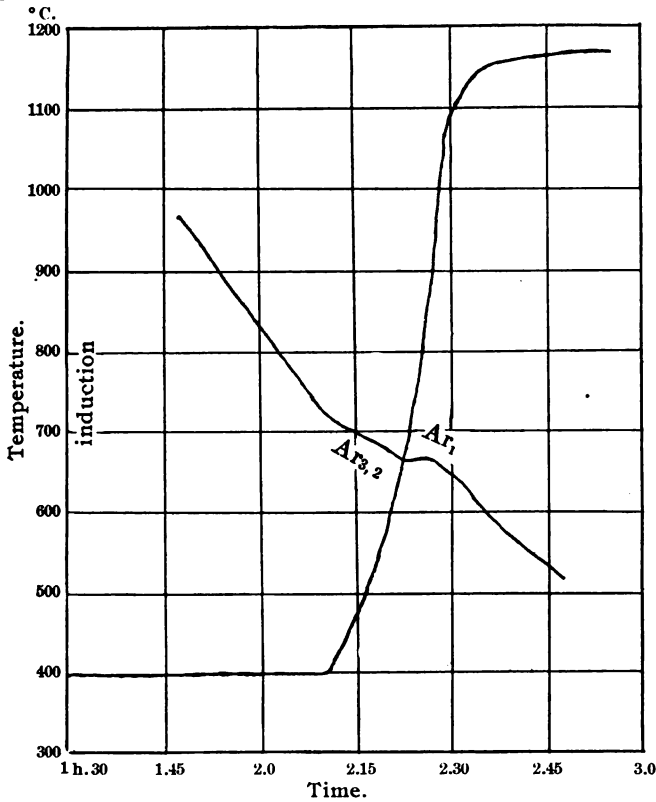

FIG. 1.

Mrs. Sklodowska-Curie has sought the conditions which were the most favorable for the preparation of magnets, but she did not take much pains to connect her researches with ours. I must, therefore, in order to establish my first proposition, turn to another physicist, Dr. J. Hopkinson, whose experiments are perfectly appropriate to my purpose. Among the steels studied by that authority,[*] I shall select the one which

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[*] *Magnetism and Recalescence.* *Proc. Royal Soc.*, Vol. XLVIII, pages 443–4.

contains about 30 per cent of carbon, and I reproduce in Fig. 1 the curves which give (as ordinates) the course of the cooling and the magnetic induction with regard to time (as abscisses). "It will be observed," says the author, "that there is a considerable liberation of heat, beginning at 2 h. 12 m., temperature 715° C., and continuing to time 2 h. 22 m., temperature 660° C., being apparently somewhat slower at the end. . . . At time 2 h. 22 m., temperature 660° C., the rate of liberation becomes much more rapid, so much so that the temperature for a time remains almost stationary. At time 2 h. 29 m. the liberation of heat appears to have ceased and the normal cooling to continue. Now, comparing the kicks of the galvanometer, all proportional to the induction, we observe that the ring begins to be magnetizable at time 2 h. 12 m., the magnetic property increases till time 2 h. 22 m., after this point the magnetizability increases much more rapidly, and is practically fully developed at 2 h. 31 m. In this case, the development of the magnetic property follows precisely the liberation of heat, observed both at the temperature of about 700° C. and at 660° C. We may, therefore, be certain that both at the higher and lower temperature of recalescence there is magnetic change, and that the one is as much dependent on the other as the solid condition of ice is upon the liberation of heat when water solidifies. The two changes occur, not only at the same temperature, but simultaneously."

In other words, the magnetic transformation begins with the beginning of $Ar_{3\ 2}$ and finishes with the end of Ar_1.

(2) *The power of hardening is not localized at the point Ar_1 in steels which possess several critical points.*

This proposition has been demonstrated by Mr. Howe.[*] Experimenting with steel bars containing 0.21 per cent of carbon and 1.19 per cent of manganese, and therefore comparable to the metal of Dr. Hopkinson (for the smaller amount of carbon is compensated by a larger percentage of manganese), Mr. Howe found a diminution of 61,673 lbs. per sq. in. in the tenacity of quenched bars, between the middle and the end of $Ar_{3\ 2}$, of 19,244 lbs. between the end of $Ar_{3\ 2}$ and the beginning of Ar_1, of 36,756 lbs. during Ar_1, and of 15,044 lbs. after the apparent end of Ar_1. These facts have been confirmed by Mr. Arnold.[†]

In other words, the transformation which confers the hardening power occupies the whole critical range.

Conclusion. — *In steels possessing two critical points, the magnetic transformation and the transformation which confers hardening power follow exactly the same course. Both transformations,*

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[*] *Journal of the Iron and Steel Institute*, No. II, 1895, page 294, and No. I, 1896, page 172.

[†] *Engineering*, July 9, 1897.

*supposing them to be separable, are not separated. They may not
be identical, but the phenomena take place as if they were.*

Corollary. — Since, on the other hand, the experiments of
Mrs. Curie and others have identified the magnetic trans-
formation with the point A_2 in pure iron, i.e., with the second
allotropic transformation of iron (which you rightly recall),
all the facts lead to the belief that *the second allotropic trans-
formation of iron* (change of γ iron into β iron) *is also the principal
cause of hardening, when it cannot take place integrally.*

The above facts and the deductions to which they lead
suppose that the transformation Ar_2 does not correspond ex-
clusively to the liberation of heat which I have designated by
that symbol, and that a portion of it belongs to Ar_1 in steels.
You will perhaps reply that I am in contradiction with my-
self, since, in my publications of 1887 and of 1890, I attributed
the point Ar_1 exclusively to the transformation of hardening-
carbon into cement-carbon. To this objection I shall simply
answer that I was mistaken, and that I must rectify an error
which I put in circulation. I did not know in 1890 what we
know to-day. Since that time, your own researches and mine
have established that a steel containing 0.30 per cent of
carbon splits up during cooling, and as soon as the critical
range is reached, in two distinct structural constituents. The
amount of ferrite increases progressively until it constitutes
about 67 per cent of the mass, while the martensite decreases
correspondingly, with a proportional concentration of carbon.

If the segregation of ferrite begins at 715° C., for instance
(to take the figures of Dr. Hopkinson), this temperature of
715° being identical to that of the point Ar_2 in pure iron and
inferior to the temperature of the point Ar_3, both transforma-
tions of the iron, which had been retarded until then by the
presence of carbon, will now take place, *but only in the ferrite*,
and as this constituent is liberated. In the martensite, the
accumulation of carbon will continue to retard the trans-
formation of the iron, postponing it until the point Ar_1. And
indeed, since martensite finally becomes identical to a hard
steel containing about 0.90 per cent of carbon, it must neces-
sarily behave like all hard steels, i.e., the three critical points
must be united in a single point. In soft steel, however, as
soon as the beginning of the critical range is reached, the
martensite occupies only, during cooling, a portion of the
mass, and, therefore, the point Ar_2 as well as the point Ar_3 is
divided into two fractions, the first one making its appearance
when it can, i.e., in the segregating ferrite, and the second
later in the martensite, when at Ar_1 the cementite segregates;
this second fraction is evidently null in pure iron; it increases
with the carbon-content and reaches 100 per cent in eutectic
alloy (with about 0.90 per cent of carbon).

I know that you have no set opinion on this subject. I hope that my demonstration will appear convincing to you, and I pray you to publish it in *The Metallographist.*
    PARIS, April 19, 1898.   F. OSMOND.

To the Editor of *The Metallographist.*
    Sir : — Replying to your question, "whether steel must necessarily be in a non-magnetic condition in order to be hardened by sudden cooling," I answer most emphatically "No."
    First, Brinnell showed long ago that, as the temperature descends, the hardening power at least of medium-carbon steel departs not abruptly, but progressively. Osmond showed how long a range is covered by the retardations of cooling, and in 1895 I showed that, in case of steel containing 0.21 per cent of carbon, the loss of the hardening power, while occurring chiefly at the critical points $Ar_{2\,3}$ and Ar_1, is spread over at least 190°C., even during slow cooling. Further, the recovery of the magnetic properties is progressive, and at least in large part occurs simultaneously with the loss of the hardening power. Hence, when part of this transformation has occurred, i.e., when part only of the hardening power has been lost, so that part also remains, the magnetic properties will have been partly recovered; and if the steel now be quenched, it will be partly hardened, or, to approach your words, the steel will be partly hardened by sudden cooling, although magnetic.
    This is clearly shown in a lecture demonstration which I have devised. Mount a magnetic needle on trunnions so that it swings in a vertical plane. Attach a piece of white asbestos to it to make it readily visible, or better a piece of luminous paper and darken the room. Heat a piece of stout high-carbon steel wire red-hot, holding it by means of a light platinum (not iron or copper) wire, hold it very near the magnetic needle: the needle remains unaffected until the wire in cooling approaches the recalescence, when the needle moves with accelerating speed toward the cooling wire, which therefore has become magnetic. If you quench the wire in water as soon as it has thus recovered its magnetism, you will find it glass-brittle. If, however, you wait a few seconds before quenching it, you will find it only slightly hardened; and if next time you wait a few seconds more, it will, if roughly tested, seem wholly unhardened. I have found this one of the most effective ways of demonstrating to a class the wonderful transformation from the high to the low temperature condition of steel.
    Thus the fact that steel will harden when strongly magnetic is to me a most familiar observation.
    NEW YORK, June, 1898.   HENRY M. HOWE.

No. 14.   Silicon Steel, 4 per cent Silicon, 0.02 per cent Carbon.
Magnified 60 diam.   Etched 30 min. in $^1|_{10}$ nitric acid.
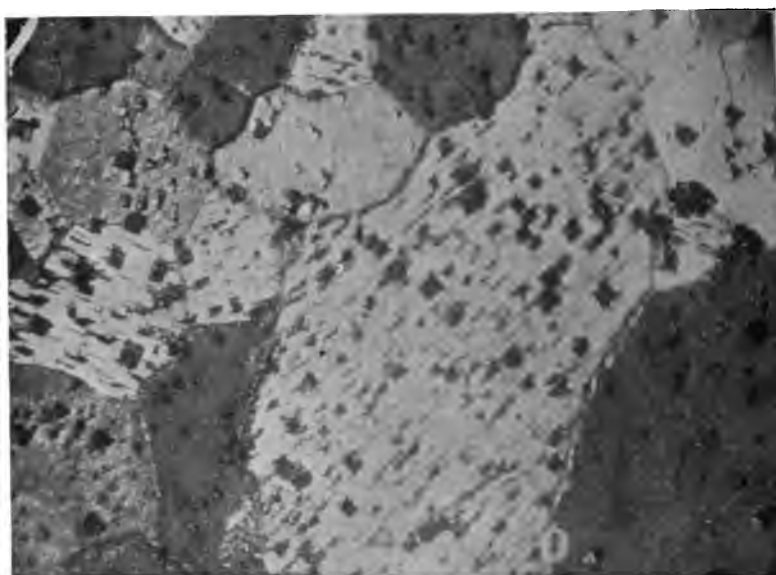
No. 15.   Silicon Steel, 4 per cent Silicon, 0.02 per cent Carbon.
Same as No. 14.
Magnified 60 diam.   Etched 120 min. in $^1|_{10}$ nitric acid.

PHOTOMICROGRAPHS OF SILICON STEEL, after STEAD.

ON THE SIGNIFICATION OF THE CRITICAL POINTS OF IRON AND STEEL.

By F. OSMOND.

I T is known that during the slow cooling of irons contain-
ing a certain amount of carbon, three different transfor-
mations take place: two allotropic transformations of the iron
itself and the transformation of hardening-carbon into cement-
carbon. Similarly three evolutions of heat are observed, dis-.
tinct in very soft steel, but which are reduced to two, then to
a single evolution, as the carbon-content increases progres-
sively.

Each evolution of heat was at first identified exclusively
with a single transformation. But this identification, which
is justified in the extreme case of pure iron, becomes less
and less justifiable as the carbon increases.

Microscopic researches, notably those of Messrs. Howe
and Sauveur, have indeed shown that in slightly or moder-
ately carburetted steels two different constituents separate
during cooling: ferrite which does not contain any carbon,
and martensite in which the carbon is concentrated. During
the critical range the proportion of martensite diminishes
progressively until its carbon-content reaches 0.8 or 0.9 per
cent: the phenomenon of the recalescence then takes place,

and martensite is transformed into pearlyte without any appreciable change of volume. In presence of carbon, however, the transformation of the iron, which takes place theoretically at about 860°C., and between 750° and 700°C., are retarded until the temperature of recalescence is reached (675° to 650°C. in pure steels). It follows from these considerations that in steels which break up into ferrite and martensite, the transformations also are similarly divided into two fractions. The first portion of the transformations takes place in the ferrite alone, as this constituent is formed; the second occurs in the martensite at the temperature of recalescence.

This consequence of micrographic researches, however, has not always been recognized, and it is evident that the primitive interpretation which *closely* identified each of the transformations with the corresponding evolutions of heat has remained alive in many minds.

It is a source of confusion, and as I am probably the principal culprit, I shall endeavor to remove it.

The best means to accomplish this purpose, I think, is to designate by different symbols the causes (i.e., the transformations mentioned above) and the effects (i.e., the evolutions of heat).

Let Ar_3, Ar_2 and Ar_1 designate, according to the usual notation, the observed evolutions of heat, in calories per gramme of metal.

Let Q_β^γ be the quantity of heat evolved by the passage of 1 gramme of iron from the γ to the β state,

Q_α^β the quantity of heat evolved by the passage of 1 gramme of iron from the β to the α state,

Qc the quantity of heat evolved during the transformation of hardening-carbon into cement-carbon in 1 gramme of martensite passing to the pearlyte state.

Then, for 1 unit in weight of steel, let

M_3 be the proportion of martensite at the end of Ar_3,

M_2 the proportion of martensite at the end of Ar_2,

M_1 the final proportion of martensite at the moment of its transformation into pearlyte;

C, the proportion of cementite corresponding to the ·

carbon-content, the transformation of the carbon being supposed to be complete.

At. the end of Ar_3, the proportion of ferrite is $1 - M_3$, and since the transformation of the iron from the γ to the β state occurs only in the ferrite, we have:

$$Ar_3 = Q_\beta^\gamma (1 - M_3).$$

At the end of Ar_2, the proportion of ferrite is $1 - M_2$; the liberation of heat Ar_2 is composed of two terms: the evolution of heat due to the change of γ into β iron, taking place in the weight of ferrite $M_3 - M_2$, set free by the contraction of the martensite since the end of Ar_3, and the heat liberated by the change from the β to the α state of the total ferrite. Therefore,

$$Ar_2 = Q_\beta^\gamma (M_3 - M_2) + Q_\alpha^\beta (1 - M_2).$$

Ar_1 includes: (1) the heat evolved by the two transformations of the iron in the ferrite $M_2 - M_1$ liberated by the shrinkage of the martensite since the end of Ar_2; (2) the evolution of heat due to the transformation of hardening-carbon into cement-carbon in the weight M_1 of martensite; (3) the heat liberated by the two transformations of iron in the ferrite $M_1 - C$ liberated by the formation of cementite, so that

$$Ar_1 = (Q_\beta^\gamma + Q_\alpha^\beta) (M_2 - M_1) + Q_c M_1 + (Q_\beta^\gamma + Q_\alpha^\beta) (M_1 - C)$$

or, in simplifying:

$$Ar_1 = Q_c M_1 + (Q_\beta^\gamma + Q_\alpha^\beta) (M_2 - C).$$

Let us see what becomes of these formulas in a few special instances.

In pure iron $M_3 = M_2 = M_1 = 0$

$$\begin{cases} Ar_3 = Q_\gamma^\beta \\ Ar_2 = Q_\alpha^\beta \\ Ar_1 = 0 \end{cases}$$

In steels in which Ar_3 and Ar_2 are united:

$$Ar_3 + Ar_2 = Ar_{3\,2} = (Q_\beta^\gamma + Q_\alpha^\beta) (1 - M_2).$$

In steels which have only one critical point:

$$Ar_3 + Ar_2 + Ar_1 = Ar_{3\,2\,1} = Q_c M_1 + (Q_\beta^\gamma + Q_\alpha^\beta) (1 - C).$$

It should be noted that Qc is probably the sum of several terms which may include (1) the heat of combination of iron with carbon, if these two elements are dissociated partly or wholly above the recalescence; (2) the heat of segregation of the cementite, if the carbide Fe_3C is simply dissolved, wholly or in part, above the recalescence; (3) the heat of transformation of the non-magnetic Fe_3C into its magnetic isomer.

Let us also notice that the point Ar_1 is never due to the carbon alone, but always includes a fraction at least, varying with the carbon-content, of the allotropic transformation of the iron. The phenomenon of hardening never is, therefore, independent of these transformations.

I hope that this note will dissipate all confusion, and subsequent discussions would probably gain in clearness if the metallurgists who hold a view different from mine, would also express their opinions under a comparable mathematical form.

MAGNETIC PROPERTIES OF HARDENED STEELS.

By Mrs. SKLODOWSKA CURIE.

Permanency of Magnetization of the Steel Bars.

VARIOUS causes may produce a variation of the magnetic condition of a magnet. The following should be especially considered:

1. The action of shocks and vibrations.

2. The action of variations in the surrounding temperature.

3. The action of magnetic fields of neighboring magnets or currents.

4. The action of time, the magnet being susceptible of spontaneous modification in function of the time.

Messrs. Barus and Strouhal* have studied this question with great care; they have shown, especially, the necessity of a long reheating at a low temperature. It has also been

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* *Bulletin of the United States Geological Survey*, 1885.

found that the magnetism is much more stable when the magnet, after having been magnetized to saturation, is partially demagnetized.* Hence the two operations which give permanency to a magnet: reheating to a relatively low temperature and partial demagnetization after saturation.

Messrs. Barus and Strouhal recognize two kinds of variations produced by the causes mentioned above: variations in the nature of the piece of steel forming the magnet, and variations of the magnetic condition of the magnet. They studied the variations in the nature of steel bars by measuring their electric resistance. For the same purpose, I have measured the coercitive field, whose magnitude characterizes very well the condition of the bar. A variation in the nature of the steel composing the magnet generally entails a diminution of the intensity of magnetization if the steel is magnetized when the variation takes place; it is necessary, therefore, that the conditions of the steel should vary as little as possible.

Effect of Reheating to a Low Temperature upon the Nature of the Quenched Steel Bars. — I endeavored to find to what extent reheating to 60°, 100° and 200° C. modifies the coercitive field and the intensity of maximum residual magnetization of bars of different nature. (See Table VIII.)

In the first series of experiments fifteen quenched steel bars of different nature were treated. The coercitive field and the intensity of residual magnetization at the center of the bar † were measured after each successive heating — the first heating lasted three hours at 100° C.; the second, seven hours at 100°; the third, three hours at 200°.

In the second series of experiments, carried on with more care, three bars only were treated. According to the results of the first series, reheating ten hours at 100° does not seem to exhaust, in the case of hard steels, the effect which such treatment is capable of producing. In the second series, the reheatings lasted in all twenty-four hours; the bars were

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* See Du Bois and E. Taylor Jones, *Electrotechnische Zeitschrift*, 1896, Heft 3.

† The intensity of magnetization referred to here is the one which remains in the bar when it has been again *magnetized* to saturation at the atmospheric temperature after each reheating.

TABLE VIII. — *Effect of Reheating.*

1st Series.

	% C.	Coercive field.				Intensity of residual magnetization.			
		Steel untreated.	3 hours at 100°.	10 hours at 100°.	3 hours at 200°.	Steel untreated.	3 hours at 100°.	10 hours at 100°.	3 hours at 200°.
Firminy carbon-steels	0.06	3.4	3.0	3.2	4.3	27	27	20	41
	0.20	11	11	11	11	116	105	119	111
	0.5	23	21	22	20	207	204	205	197
	0.84	51	47	48	29	394	391	386	295
	1.2	58	56	55	33	445	434	426	334
Unieux carbon-steels	0.96	54	51	51	35	382	374	363	337
	1.40	58	57	56	27	353	354	348	251
	1.41	60	58	57	29	361	356	347	258
	1.61	46	45	44	26	270	264	266	223
Allevard steel . { Bar 1		73	70	68	44	552	543	542	449
{ Bar 2		72	69	68	34	562	548	548	374
Boehler special steel, very hard		74	69	68	37	572	557	553	422
Boehler Boreas steel . . .		85	80	78	55	385	385	386	434
Molybdenum-steels . { B		85	79	78	30	512	509	502	327
{ C		73	70	69	47	442	434	437	406

2d Series.

	Carbon-steel C = 0.84 %.		Allevard steel.		Molybdenum-steel C.	
	Hc	Ir	Hc	Ir	Hc	Ir
Steel, untreated	51	422	69	574	79	429
Steel, reheated 3 hours at 100° .	45	415	65	583	73	433
do. do. 10 hours at 100° .	45	396	63	549	71	418
do. do. 16 hours at 100° .	44	397	62	544	70	416
do. do. 24 hours at 100° .	44	390	61	540	70	413
Steel after 8½ hours of further reheating at 150°	37	363	46	465	50	417
Steel after 7½ hours of further reheating at 200°	28	310	37	401	40	382
Total loss % after reheating at 100°	13	8	·12	6	12	4
do. do. do. do. at 200°	41	27	47	33	50	11

3d Series.

	Allevard steel 1st bar.		Allevard steel 2d bar.		Boehler Boreas steel.		Molybdenum-steel B.	
	Hc	Ir	Hc	Ir	Hc	Ir	Hc	Ir
Steel, untreated	70.7	561	70.7	579	79.8	336	82.5	496
Steel, reheated 7 hours at 60°	69.7	572			78.3	340	79.7	494
do. do. 42 hours at 60°	69.9	564			79.0	339	79.8	490
do. do. 52 hours at 60°			69.6	579				

then subjected to further reheatings, lasting eight hours and a half at 150° and seven hours at 200°. These reheatings are probably sufficient to exhaust the possible effect of reheating at such temperatures. Messrs. Barus and Strouhal have, indeed, shown that the time required for the completion of the effect produced by reheating is the shorter the higher the temperature. In a third series of experiments a few bars were treated in order to ascertain the effect of reheating to 60°.

In the case of steel with 0.06 per cent of carbon, the coercitive field was found greater than when the bar was reheated to 200°.

With 0.2 per cent of carbon in the steel, the magnetic constants vary little after reheating to 100° or to 200°.

With 0.5 per cent of carbon the coercitive field is slightly reduced by reheating.

In the case of all hard steels, reheating to 100° is sufficient to greatly reduce the coercitive field; the diminution reaches from 12 to 13 per cent in the case of carbon-steel with 0.84 per cent of carbon, of the Allevard steel and of a sample of molybdenum-steel; it should be stated, moreover, that in the case of the last two bars, the effect of reheating did not seem to be completely exhausted after twenty-four hours' treatment.

Reheating to 200° reduces much more still the coercitive field of hard steels, the diminution amounting to 41 per cent in the case of the sample containing 0.84 per cent of carbon, to 47 per cent for the Allevard steel and to 50 and 65 per cent, respectively, in the case of two different molybdenum-steels.

It follows from these experiments that reheating, even at a low temperature, diminishes the coercitive field of hard steels in a proportion which is the greater the better suited the steel for the construction of magnets. Magnets should not be reheated to 200° C. in order to be made permanent, for the metal loses then 50 per cent of its coercitive field, and its magnetic qualities are considerably altered. Reheating to 100° causes a diminution of the magnetic field amounting to 12 or 13 per cent; it is therefore already very injurious, for it involves a corresponding and very appreciable diminution in the stability of magnetization.

It would seem that, in practice, we must be satisfied with a somewhat long reheating (24 hours, for instance) at 60° or 70°; the resulting diminution of the coercive field does not, then, exceed 3 per cent in the case of hard steels.

The intensity of residual magnetization is also altered by reheating, but it is a complex quantity, and the results obtained would have been very different if bars of a different shape had been used.* In the case of a certain shape, for instance, the intensity of residual magnetization may remain invariable while the properties of the steel are profoundly modified.

The bars examined were 20 cm. long, with a cross-section 1 cm. square, except those of Unieux steel, containing 1.40, 1.41 and 1.61 per cent of carbon, which had a cross-section 0.83 cm. square.

In the case of the soft carbon-steels, containing respectively 0.06, 0.2 and 0.5 per cent of carbon, the intensity of magnetization varies as the coercive field: with 0.06 per cent of carbon in the steel, it increases by reheating at 200°; it remains invariable when the steel contains 0.20 per cent of carbon, and diminishes a little with a carbon-content of 0.5 per cent.

The intensity of magnetization of hard steels diminishes, generally, on reheating, but not as much as the coercive field. In the case of certain steels with a high coercive field, the intensity of residual magnetization remains constant or even increases, on reheating, while the coercive field undergoes a marked diminution. We must conclude from these facts, that, with such steels, the intensity of residual magnetization of a closed circuit must increase considerably on reheating. The intensity of magnetization of Boreas steel bars, for instance, remains constant after reheating to 100°; it increases on reheating to 200°, while the coercive field is greatly decreased.†

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* Barus and Strouhal, *loc. cit.*

† From what precedes, it seems probable that soft steels would be sufficiently hardened if the quenching bath had a temperature of 150° or 200°; high-carbon steels, on the contrary, would not, in these conditions, be hardened enough.

Action of Shocks and Vibrations on the Magnetic Condition of a Bar Magnetized to Saturation. — The shocks were produced by falls. The bar was first placed vertically and allowed to fall from a height of 85 cm. upon a block of hard sandstone; it was then held horizontally and allowed to fall on the same stone from a height of 30 cm. These falls were then alternately repeated. They do not modify the nature of the steel bar, for its coercitive field and its power of magnetization remain the same. We must, therefore, ascertain the effect of such treatment upon the magnetic condition of the bars. With that end in view the intensity of magnetization at the center of the bar was measured, two minutes or so after it had been magnetized to saturation;* it was then made to fall as described above, and the intensity of magnetization of the bar ascertained in the interval between the falls. The first falls are the most effective, the following ones producing an effect less and less marked; the intensity of magnetization approaches asymptotically a constant value smaller than the initial value.

The phenomenon, however, is not always as regular; it sometimes happens that after a few ineffective falls the succeeding ones still produce a small diminution of the intensity of magnetization, as if a new small group of magnetized particles had been reached by the shocks.

The results of some experiments conducted with bars of various kinds will be found in Table IX. Only the results obtained with bars having the same dimensions are comparable with each other. The table shows the percentage of total loss after the action of the falls has been exhausted.

In the case of very soft steel, containing from 0.06 to 0.2 per cent of carbon, the percentage of the loss of magnetization is very great. The number of falls required to obtain a magnetization practically constant is, moreover, so great that

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* After a bar has been magnetized to saturation it loses spontaneously, during a few minutes, a small part of its magnetization. The phenomenon is perceptible only in the case of steels with a weak coercitive field; but the magnetization of such steels varies under the influence of the slightest shock, and it is not possible to tell whether the loss, apparently spontaneous, is not due to the inevitable vibrations and slight shakes.

I did not try to reach it. Generally speaking, the total loss by falls is the smaller, the greater the coercive field (see Table IX). The intensity of magnetization, however, also

TABLE IX. — *Loss of Magnetization Caused by Successive Falls.*

	Bars not reheated.				Bars reheated to 100°.			Bars reheated to 200°.		
	Hc	Ir	Loss of magnetization per cent	Number of active falls	Hc	Loss of magnetization per cent	Number of active falls	Hc	Loss of magnetization per cent	Number of active falls
Bars 20 cm. long, 1 cm. square.										
Per cent.										
Carbon-steels { C = 0.06	3	27	>83	>75						
C = 0.2	11	117	>45	>95						
C = 0.5	23	210	23	30	22	20	20	20	24	80
C = 0.84	54	398	3.2	15						
C = 0.96	54	386	3.4	20						
C = 1.2	58	451	4.8	20						
Allevard steel I .	72	570	6.0	45						
do. do. II .	73	560	5.0	50	68	7	100	44	9.2	60
Molybdenum-steel C	73	448	2.9	10	69	3	30	47	7	100
Special Boehler steel, very hard	74	580	3.0	20						
Molybdenum-steel B	85	520	3.2	10						
Boehler Boreas steel	86	390	1.5	5				55	3.7	20
Bars 20 cm. long, 0.85 cm. square.										
Per cent.										
Carbon-steels { C = 1.40	59	358	3.5	15						
C = 1.41	60	366	5.5	20						
C = 1.61	46	274	8.5	20						
Allevard steel . .	74	680	2.6	10						

exercises some influence; for the same coercitive field, the percentage of loss due to falls is the greater, the greater the intensity of magnetization. The Boehler-Boreas steel, for instance, which has a high coercitive field and an intensity of magnetization relatively low, loses less by falls than any other sample examined.

The number of effective shocks have been tabulated in Table IX, i.e., the number of shocks required for the inten-

sity of magnetization to reach a constant value in the case of given falls, similar falls producing no longer any appreciable effect. It may be inferred from the nature of the phenomenon, that this number of falls is not a well-defined quantity; its approximate value, however, gives an idea of the rapidity with which the intensity of magnetization assumes its new value, in the case of various bars. It is seen that, in general, the new value is reached the soonest when the falls have the least effect. In this respect, however, there exist some individual differences between the bars. It will also be noticed, that in the case of hard steels the limit is quite rapidly reached.

The shocks referred to, here, were quite severe (causing the fracture of some bars); after the stable condition had been reached, the magnet could be struck heavily in various directions, by means of a copper hammer, without further variations.

As the pieces of steel which are used for the manufacture of permanent magnets must be reheated at a low temperature, it was interesting to ascertain the influence of the falls after reheating and magnetization (Table IX).

The character of the phenomenon is not changed. The percentage of loss of the intensity of magnetization by shocks is greater after reheating; it is a natural consequence of the diminution of the coercitive field.

Effect of Shocks on Magnetized Bars Partially Demagnetized. — The shocks were produced by falls similar to those just described.

Experiments with a Magnetized Bar of Allevard Steel 20 cm. long, with a cross-section 85 cm. square.

	Intensity of Magnetization.
Bar magnetized to saturation	676
After a great number of falls	658
Bar again magnetized and then demagnetized in a field of 6.4 units	660
After a great number of falls	656
Bar again magnetized and then slightly demagnetized in a field of 14 units	632
After a great number of falls	632

The falls have no longer any appreciable effect.

Experiments with a Bar of Carbon-steel containing 0.5 per cent of Carbon, 20 cm. long and 1 cm. square.

	Intensity of Magnetization.
Bar magnetized to saturation	200
After a great number of falls	152
Bar again magnetized and then demagnetized in a field of 8.5 units	150
Still losing by further falls.	
Bar again magnetized and then demagnetized more strongly in a field of 13.8 units	118.4
The magnetization increases then spontaneously, after 4 days it has become nearly constant	123
Further falls no longer have any appreciable effect.*	

It appears, therefore, that by demagnetizing the bars partially, the effect of the falls is less and less marked. The Allevard bar becomes completely insensible to the falls when the demagnetization reaches about six per cent of the intensity of magnetization in the saturated condition. In the case of the soft-steel bar it was necessary to carry the demagnetization to 40 per cent to render the steel insensible to further falls. It is therefore possible, through a partial demagnetization, to cause the magnetization of steel bars to remain unaffected by shocks. The method is evidently less dangerous for the bar and simpler than the one consisting in allowing the bar to fall many times from a certain height. In the case of various quenched bars of *high-carbon steel* having a length of 20 cm. and a cross-section of 1 cm. square, I constantly found that a demagnetization amounting to $\frac{1}{10}$ of the maximum magnetization was more than sufficient. The bars

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* When a bar is partially demagnetized, it has a tendency to resume gradually a part of its primitive magnetization; this progressive increase is hardly noticeable in the case of bars of hard steels which have only been demagnetized to the extent of one tenth of their magnetization. With soft steels, however, which have been strongly demagnetized, the phenomenon of spontaneous increase of the intensity of magnetization is very apparent. The following results were obtained with the bar of quenched steel containing 0.5 per cent of carbon:

Bar magnetized to saturation, I = 200. Bar partially demagnetized the 3d of June in a field of 13.8 units gave, immediately after demagnetization, I = 118.4; the 5th of June, I = 120.8; June 6th, I = 122.3; June 7th, I = 122.9.

thus slightly demagnetized may be subjected to violent vibra-
tions without losing any of their magnetization.*

*Influence of Reheating at a Low Temperature upon the
Condition of Magnetization of a Magnetized Bar.* — By heating
some magnetized bars, it is possible to study the alterations
produced by variations of the surrounding temperature.

The following results were obtained in the case of four
bars of hard steels, quenched and magnetized to saturation
and then heated for 10 minutes at 60° C.

	Intensity of Magnetization	
	Before Heating.	After Heating.
Bar of carbon-steel (C 0.84 per cent) . .	394	387
Allevard steel A	562	541
do. do. B	523	517
do. do. C	580	568

It is seen that all the bars have lost a part of their mag-
netism. The period of heating, however, having been very
short, the steel did not undergo any modification that could
be detected by the measuring instruments used. The coerci-
tive field of the bars had not varied, and, by again magnetiz-
ing them to saturation, the original intensity was recovered.
One of the Allevard bars had previously been subjected, after
quenching, to a prolonged reheating at 60° C. A bar mag-
netized *to saturation*, therefore, loses a part of its magnetiza-
tion upon being reheated for a few minutes at 60° C., even if
it has been previously reheated to that temperature. It is,
consequently, absolutely necessary to use bars which have
not been magnetized to saturation if it is desired that their
magnetization should remain unaffected by the surrounding
temperature.

A few experiments were conducted with bars having
at their center about $\frac{9}{10}$ of their maximum residual mag-
netization.

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* It should be stated, however, that the direct demagnetization of
the bar must be greater than the one resulting from falls, in order to
render the bar insensible to subsequent vibrations. The two methods of
demagnetization are not, therefore, absolutely equivalent, and, if it was
desired to construct some standard magnets of great precision, it would
be advisable, after the partial demagnetization, to subject the magnet to a
few falls.

The bar of Allevard steel D, quenched but not reheated ($H_c = 70.7$), was magnetized to saturation ($I_r = 580$), then partially demagnetized in a field of 13 units; its intensity of magnetization is then $I = 528$ (about 0.9 of the original magnetization).

In these conditions the magnetization was found much more stable, remaining unaffected by falls from a height of 80 cm. After reheating at 60° C. for ten minutes, the magnetization remained practically constant, $I = 527$; but after a prolonged reheating (52 hours) at 60°, it showed an appreciable diminution, $I = 510$; the coercive field was then $H_c = 69.6$. The same treatments were then repeated. The bar was again magnetized to saturation ($I_r = 580$) and partially demagnetized in a field of 12 units; the intensity of magnetization was then $I = 519$; after successive reheatings at 60° C. lasting respectively 8, 6 and 17 hours, the intensity was found to remain practically constant, its value after each reheating being respectively $I = 519.3$, $I = 519$, $I = 520$.

It is seen, then, that when the bar (Allevard steel, quenched but not reheated) has been magnetized to saturation and demagnetized to the extent of $\frac{1}{10}$, a long reheating at 60° makes it lose a portion of its magnetization, but that such is not the case if the bar, after quenching, is reheated to 60°, magnetized to saturation and demagnetized to the extent of $\frac{1}{10}$; repeated heatings to 60° no longer modify, then, the intensity of magnetization.

It is possible that if the bar was more strongly demagnetized a preliminary heating of 60° would not be necessary.

Below are some experiments made with two other bars of hard steel (Allevard bar E, molybdenum bar B).

These two bars were quenched and then reheated to 60° for 7 hours. The bar E was then magnetized to saturation: $I_r = 573$; partially demagnetized in a field of 14 units: $I = 508.8$; after heating 33 hours at 60°: $I = 509$.

The bar B was also magnetized to saturation: $I_r = 493$; partially demagnetized in a field of 20 units: $I = 444.2$; after heating 23 hours at 60°: $I = 445.6$; after a further heating of 16 hours at the same temperature: $I = 444.5$.

Variation of the Intensity of Magnetization of Magnetized Bars, with the Temperature. — A quenched bar of high-carbon steel, reheated to 60°, magnetized to saturation and demagnetized to the extent of one-tenth of its maximum residual magnetization possesses a magnetization which has always the same value for a given temperature, even after various fluctuations of the surrounding temperature. While examining the magnetization of the bar at various temperatures, on the

contrary, it is found that the magnetization is a little smaller when the temperature is higher than the surrounding temperature, and a little greater when the temperature is lower. In other words, there exists a coefficient of variation of the intensity of magnetization with the temperature, and that coefficient is negative.

The differences are very small and difficult to measure with the instruments used.

Here are, for instance, a series of experiments conducted with the Allevard steel bar D and the molybdenum bar B. The intensity of magnetization at the center of the bar is tabulated and expressed in arbitrary units.

ALLEVARD BAR.

				Magnetization.
Maximum residual magnetization	. . . . . .			36.5
	1st series		at 17°	32.06
			at about 45°	31.88
			at 17°	32.08
Bar demagnetized in a field of 13 units.			at 17°	31.81
			at about — 10°	31.99
			at 17°	31.83
	2d series		at about — 10°	31.99
			at 17°	31.82
			at about 45°	31.68
			at 17°	31.81

MOLYBDENUM BAR.

		Magnetization.
Maximum residual magnetization	. . . . . .	31.17
	at 17°	27.66
	at about 45°	27.50
Bar demagnetized in a field of 21 units .	at 17°	27.67
	at about — 10°	27.93
	at 17°	27.66

From these experiments it is only possible to calculate the magnitude of the coefficient of variation of the magnetization with the temperature. In the case of the Allevard steel it is found to be 0.0002, while with the molybdenum-steel its value is 0.0003; variations amounting to $\frac{1}{400}$ of the intensity of magnetization of a bar could, therefore, occur for a variation of 10° in the temperature. The coefficient of variation may possibly depend also upon the shape of the bar and its condition of magnetization. The bars examined were 20 cm. long and had a cross-section 1 cm. square.

Variation of Magnetization Produced by External Magnetic Actions. — In order to modify the intensity of magnetization of a bar to the extent of a given fraction of its value, it is, in general, necessary to operate in a field which is the greater the stronger the coercitive field of the bar. In order, for instance, to permanently demagnetize to the extent of $\frac{1}{10}$ some bars possessing their maximum residual magnetization, it was necessary to place them for one instant in the following fields:

	Coercitive Field.	Demagnetized in a Field of
Carbon-steel, C 0.5 per cent	21	· 3.5 units
Allevard steel reheated to 60° . . .	70	13.5 do.
Allevard steel not reheated	71	13.0 do.
Boreas steel reheated to 60°	78	27.5 do.
Molybdenum-steel B reheated to 60° . .	80	21.0 do.

The field required by the Boreas steel is remarkably intense.

The four last bars having been magnetized to saturation, then demagnetized to the extent of $\frac{1}{10}$, I ascertained what would be the disturbing and permanent influence of a magnetic field acting temporarily in one or the other direction. I found that when the fields were weaker than that which had served to demagnetize, the variation in the intensity of magnetization amounted to between 0.1 and 0.3 per cent, while with more intense fields the variations were quite considerable. The variations, for instance, remain inferior to 0.3 per cent when the disturbing field does not reach 13 in the case of the Allevard steel, 27 in the case of the Boreas steel and 21 when operating with the molybdenum-steel B. If the bars are demagnetized more than $\frac{1}{10}$, the field which served to demagnetize is higher, as well as the disturbing field for which the variations become considerable; on the other hand, in the case of weak fields, the variations are then greater. With an Allevard bar, for instance, demagnetized successively to the extent of 0.37 and 0.64 of its maximum residual magnetization (the demagnetizing fields being, respectively, 40 and 68 units), a disturbing field of 7 units causes permanent variations amounting, respectively, to 0.3 and 0.6 per cent.

A method which yields good results, whatever the value

of the demagnetization, consists in demagnetizing partially by placing the bar successively in fields of opposite direction, and which have a progressively decreasing absolute value. By operating in this way the bar will vary less than previously under the influence of weak fields.

This kind of demagnetization might be produced through the action of a field generated by a coil traversed by alternating currents whose intensity would be made to diminish slowly, by means of a rheostat, until it is nil.

Constancy of the Condition of Magnetization of the Bars. — The magnet which was most used as standard in the present experiments remained constant within $\frac{1}{300}$ of its value during 15 months. It had been constructed and magnetized several years ago, and had been used for various experiments. When protected against vibrations and external magnetic influences it was found to remain constant. It does not follow, however, that it would not vary if exposed to a more intense or more prolonged heating than those to which it had been subjected during the past year, or under the action of a shock.

In order to protect a magnet, as far as possible, from actions of this kind without causing too great a loss of its magnetic intensity, it should be reheated, after quenching, to a temperature of only 60° or 70° C., for quite a long time, 48 hours, for instance; it should then be magnetized to saturation and finally partially demagnetized.* In the case of bars 20 cm. long, with a cross-section 1 cm. square, $\frac{9}{10}$ of the maximum residual magnetization may be retained; under these conditions, the magnet may be submitted to violent shocks and to variations of the surrounding temperature without any noticeable alteration of its magnetization. The conditions would be more favorable still if the bar had been

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* Messrs. Barus and Strouhal recommend to reheat the bar a first time, to magnetize it, and then to reheat it a second time. The main effect of the last operation is to demagnetize the bar a little; it may, I think, be replaced by a partial demagnetization at the atmospheric temperature. As it has already been stated, however, in the analogous case of partial demagnetization by shocks, the two methods of demagnetization may not be absolutely equivalent, and if it was desired to construct standard magnets of great precision, the partial demagnetization at the ordinary temperature should be followed by a reheating to 60° C. of the bar in its magnetized condition.

demagnetized to a greater extent, but the magnetization is always liable to vary under the influence of external magnetic fields.* The magnet may be so treated, however, that fields weaker than 5 units produce only variations smaller than 0.2 per cent, while the variations due to fields of less than 16 units do not reach 1 per cent. At all events, the vicinity of another magnet should be avoided with the greatest care — a pole of 500 units at a distance of 10 cm. is sufficient to exert a dangerous influence.

The above statements, however, should be made with some reservations. Even after the magnet has been subjected to the treatment indicated, it could not be affirmed that it will not vary under the action of a shock, even if it be smaller than those previously applied, or under the influence of a variation of temperature less considerable even than the variations to which it has previously been submitted.† All that can be said is that the probability that the magnetization will not vary has become very great. It would be illusive to seek to obtain an absolute stability with regard to vibrations or to given variations of temperature, because a perfectly stable state of equilibrium corresponds only to the non-magnetic condition.

Finally, the possible influence of time should be ascertained, as it may slowly modify the properties of the magnet from the time of its construction. Upon that subject I have only a few incomplete experiments of too short duration.

The Allevard bar D was quenched and reheated to 60° for 52 hours towards the end of July. The 31st of July its coercive field was 69.6, and its maximum residual intensity 586. September 16th the coercive field was 69.7, and the maximum residual intensity after being again magnetized 584. The magnetic constants of the bar had not varied in one and a half month.

During that interval of time, from July 31st to September 16th, the bar remained magnetized. A magnetization amounting to about nine-tenths of the maximum residual magnetization, or 520.5, was imparted to the bar July 31st; August 2d it amounted to 521.5, September 8th to 522.4, and September 16th to 523.2. The intensity of magnetization appears to have increased progressively, the increase, however, being hardly noticeable by the experimental method used.

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* See page 286.

† See page 279, influence of successive shocks.

Similarly, the Allevard bar E, the molybdenum bar A and a Boreas bar, quenched and reheated to 60° C. August 1st, were the next day magnetized to saturation and demagnetized so as to retain about nine-tenths of their maximum residual magnetization, and were then kept in that condition. In the case of the Allevard bar E, the intensity of magnetization was, August 2d, 505.5; September 8th, 509.5; September 17th, 508.8. The intensity of magnetization of the molybdenum-steel was 444, August 2d; 446, September 8th; and 446, September 17th. The intensity of the Boreas bar was 307, August 2d; 308.4, September 8th; and 307.8, September 17th.

It would seem, from the foregoing, that during the first few months after reheating, the magnetic constants (coercitive field, maximum residual intensity after being again magnetized) of the bars do not vary.

After the bars have been magnetized to saturation and demagnetized so as to retain $\frac{9}{10}$ of the maximum value of the residual intensity, the magnetization remains constant during the first few months; there seems to be, however, during the first few days following demagnetization a small, progressive increase of the intensity. It is, in a less degree, like the phenomenon which is so marked in the case of magnets slightly carburized and partially demagnetized. (See footnote, page 282.)

THE CRYSTALLINE STRUCTURE OF IRON AND STEEL.[*]

By JOHN E. STEAD.

THE crystalline structure of iron has had little attention paid to it since the early days of the metallurgy of steel.

Wohler,[1a][†] according to Dr. Percy, obtained cubic crystals on breaking cast-iron plates which had been long exposed to a white heat in the brickwork of an iron smelting furnace, and obtained also octahedral crystals in the cavities of a large unsound cast iron roll.

Dr. Percy[1b] also refers to a flat bar of iron which had been allowed to remain for a long time in a pot of molten glass, in which he found the cleavage planes arranged perpendicularly to the external surface. The surface of this bar was covered

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[*] Iron and Steel Institute, May meeting, 1898.
[†] The small figures and letters refer to the references in the Bibliography.

with fine hexagonal markings, suggesting a columnar struct-
ure. It is to be noted, also, that the greater part of the sur-
face was covered with black scale : a clear evidence of external
oxidation.

The same authority quotes Professor Miller of Cambridge,
who found Bessemer iron to consist of an aggregation of small
cubes. " The crystals," he remarks, " are very imperfect,
as might be expected, in consequence of their not having
room to develop their faces;" yet he informs us he thinks
there can be no doubt of their form, some of them being meas-
urable and giving angles approximating to 90°. This Besse-
mer iron, Dr. Percy believed, was quite free from carbon.

Referring to impurities in iron and their influence on the
form of the crystals, he says that the proportion of foreign
matter in comparison with the iron was very small, and there-
fore was not likely to change the crystalline structure.

Fuchs[1] believed that wrought iron crystallized in the
cubic system, and that cast iron belonged to the rhombohe-
dral system, and that steel was an alloy of the two systems,
the proportions varying with the temper, the harder the steel
the greater the amount of rhombohedral crystals. He stated,
that " the two kinds of iron in steel may be regarded as in a
state of constant mutual tension, which may perhaps be the
reason why steel retains permanently communicated magnet-
ism, whilst malleable iron does not." This sentence is a
clear foreshadowing of the modern theories as to the existence
of two allotropic varieties of iron, but the evidence brought
forward is not sufficiently strong to support the theory as to
the existence of a rhombohedral form of iron.

Chernoff[2] and Brinell[3] have both carefully studied the
granular structure of steel, and the effect of heating and cool-
ing upon the structure as revealed by the fracture. Chernoff
gives an excellent drawing of the forms assumed when steel
is heated to a high temperature, and clearly shows that the
so-called crystals are most irregularly shaped polygonal
masses, quite devoid of any definite crystalline form. Similar
forms I have frequently met with, and although some of the
angles undoubtedly are of 90°, it does not *per se* prove that
they belong to the cubic system. Some of the angles ex-
hibited on the fractured surface of almost pure Bessemer iron

measure 90°, but there are a greater preponderance of angles more or less acute.

Since the introduction of the study of the microstructure of iron by Dr. Sorby,[4] he, followed by Professor Martens,[5] Mr. F. Osmond,[6] Professor Arnold,[7] Mr. Thomas Andrews,[8] Mr. A. Sauveur,[9] and others, has given us a view of the structure of iron from a different standpoint. They have shown that all specimens of iron and steel are built up of granules which may have either great or small dimensions, and that the slightly etched polished surfaces of such material exhibit, when microscopically examined, polygonal figures of no constant form. Sometimes in the same microscopic field may be seen figures having from three to as many as seven sides, and with the angles varying apparently erratically. We are forced, then, to conclude that such markings do not give any clue to the crystalline form of iron, and have no relation whatever to the true crystalline structure.

We are at this point brought to face the question as to whether it is advisable to call them crystals. In mineralogical nomenclature " the leading property of crystals, as distinguished from mere geometrical solids, is the invariability of the angles between corresponding faces in different individuals of the same substance." (Bauerman's *Systematic Mineralogy*, p. 7.)

When crystals in minerals have been produced under conditions which prevent the free development of their forms, the mass in which they are imbedded is called " a crystalline aggregate," and the term " granular" may be used to describe them ; and therefore it would be more appropriate to describe polygonal bodies in iron and steel as grains, and the mass as an aggregate, coarsely, medium, or finely granular, so as to distinguish them from the crystals of which they are built. If this view is accepted, much confusion and misunderstanding will be avoided. It is the view taken by Mr. Osmond, for, in discussing the question in his excellent work on the Microscopic Analysis of Carboniferous Steels, he says : " Iron is a mass of globules more or less welded, which present an apparent tendency to group themselves in margarites and layers. Its mass is subdivided into jointed polyhedrons. When the temperature has not been too high, these forms are

regular enough, and one can easily recognize in them those of the pentagonal dodecahedron. Are the polyhedrons in question crystals or grains? Are their surfaces of contact cleavages or joints? The answer does not appear to me to be doubtful. The mass may be crystalline, but the envelopes are not. Forms exactly similar are obtained by synthesis, by compressing plastic spheroids in a mould. The desiccation of damp pastes, the solidification of melted materials, equally produce analogous divisions."

Professor Thurston, in discussing the appearance of the fracture of a hammer which had been left all night at a high temperature in an air furnace, says that "In this example the faces were nearly all pentagonal, and were usually very perfectly formed;" and judging from this fact, he considers it unmistakable evidence of the fact that iron may crystallize in the cubic or a modified system; but judging from the appearance of the diagram given by Mr. Thurston, it would not appear that they were true crystals, but in reality grains. Professor Thurston admits that granular structure is confounded with real crystallization.

In the remarks which follow, then, the polygonal forms in steel and iron will be described as grains, and the forms of which the grains are built as crystals.*

Granulation Produced on the Solidification of Metals.

The first, and by far the most simple example of granulation or the formation of grains, is that to be met with when metals solidify from the liquid state. It is well known that if the rate of cooling at the freezing-point is retarded, the metal when solid will have a coarsely granular structure, and that a structure finely granular is the result of rapid cooling. What is the cause of this difference? The same law obtains which determines the size of the individual crystals formed when hot saturated solutions of chemical salts are cooled quickly or slowly. In cooling slowly the crystals commence

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* As there is such close analogy existing between metals and rocks, as far as possible existing mineralogical terms should be adopted in discussing the structures of the former.

to grow from comparatively few points, and develop from these points only ; whereas, when heat is rapidly abstracted, the number of crystalline centers is enormously increased, and the resulting crystals are small. In the case of salts dissolved in boiling water to saturation, when they fall out of solution, whether quickly or slowly, they are comparatively free to develop their true crystalline forms, because their environment, the solvent, does not itself crystallize. In the case of pure metals, the whole mass eventually solidifies ; but just as with the salt solutions, crystals commence to grow from a few or many starting-points or centers, according to whether the cooling is slow or rapid. What follows it is easy to see. A crystal in its growth in the fluid mass develops in all directions, but its growth is at once stopped when it meets other growing crystals at the points where contact is effected ; but it is free to grow, and continues to grow in other directions until the growth of other crystals eventually completely arrests its further development.

The truth of what has been stated is very beautifully exemplified in the solidification of metallic lead. If a small quantity of lead, a few degrees above its freezing-point, is carefully skimmed, and is poured upon a flat surface, the progress of solidification can be seen to start from many quarters, and many of the points where the growing crystals meet can be seen without microscopic aid. If, when quite cold, this little tablet of lead is immersed in a dilute solution of nitric acid (1 part acid of 1.42 specific gravity to 19 parts of water), and is allowed to remain there for several hours, the surface, which was originally smooth and bright, will be found to have developed upon it most beautiful granular markings ; and if the precaution had been taken to mark the points where it was observed two or more growing masses joined in solidifying, it will be found that these points clearly show on the etched surface as granular junctions. The appearance of lead etched in this way is similar to an etched surface of soft steel. Photographs Nos. 1, 2, 6 and 7 clearly show this. The appearance of dark and light areas does not indicate different constituents, but a difference in the phase or orientation of the true crystals of which each separate granule is composed. When the object illuminated obliquely is

revolved horizontally, the grains which are light or dark in one position become dark and light respectively in another, and grains flash out brightly or become dark, and are again quenched and become dark or bright again, when a complete revolution is effected. Mr. Osmond describes this effect as resembling the flashing, revolving light of a lighthouse. There is a close relation existing between the orientation of these grains and the structural strength of the mass, as we shall see presently. The cause of this peculiarity is self-evident. The etched grains have their surfaces more or less dissolved away, but not equally so, for, on examining them under high magnifying power, they are found to have the appearance of the edges (very much serrated) of very fine lamellar plates, which dip over the whole area of any given

DIAGRAM A.
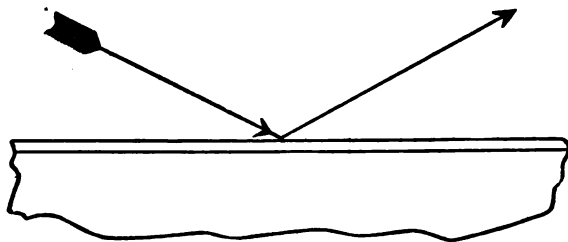
grain in one and the same angle, but at widely different angles in contiguous grains. (Photograph No. 1.)

If such a specimen is examined by allowing a ray of incident light to fall upon it, whenever it strikes the exposed flat surfaces of the crystals it will be reflected at an angle with the surface equal to the angle of incidence (Diagram A), and if the eye is in the line of the reflected ray it will of course appear bright. A slight movement of the specimen will of course alter the angle of reflection, and the ray of light will then pass away from the eye, and the grain will become dark, but the edges of the lamellæ of other grains will by the movement come into the proper position for reflection, and they will appear bright.

Professor Arnold[7b] first described the same peculiar appearance in gold, and Mr. F. Osmond's beautiful photographs

No. 1.   Carbonless Pure Iron.
Part of a single grain, showing serrated edges of crystals.
Magnified 100 diam.   Etched 5 min. in $^1|_{10}$ nitric acid.

No. 2.   Wigan Saniter Soft Steel, 0.11 per cent Carbon.
Annealed in a slag ball.
Magnified 130 diam.   Etched 1 min. in $^1|_{10}$ nitric acid.

illustrating the paper by Professor Roberts-Austen[12] and him-
self on gold alloys clearly show the edges of what appear to
be serrated laminæ pitched at various angles.

Judging from the regular way in which the light is re-
flected from the surface of each grain, there can be no doubt
that the reflecting edges are related to the crystalline structure.

It has been necessary to refer to crystallization in passing
so as to account for the peculiar behavior of different gran-
ules to incident light. We now return to the discussion of
granulation produced and destroyed by heat treatment of the
solid steel.

Granulation in Forged Steel and Iron.

In the conclusions of the paper of Brinell[8] on textural
changes effected in steel by heating and cooling (which is one
of the most valuable contributions to metallurgical science,
and should be in the hands of all workers in steel) he says:

" 1. Whenever steel loses its coarsely crystalline texture
otherwise than by mechanical elaboration, this change of
texture will always be found to occur simultaneously with the
transformation of cement-carbon into hardening-carbon, or
vice versa, and the disappearance of the coarsely crystalline
texture is solely attributable to the change of condition of the
carbon."

" 2. The coarsely crystalline texture will only disappear
to any considerable extent if a transformation of carbon takes
place in the course of heating, and will disappear altogether
only in the event of the carbon being converted by heat from
cement-carbon into hardening-carbon. In full accordance
herewith, a steel which is quite coarsely crystalline, whether
hardened or unhardened, will lose this texture altogether as
soon as its heat has attained a degree sufficient for the con-
version of ' cement ' into ' hardening ' carbon."

" 3. In order to effect the transformation of hardening-
carbon into cement-carbon in a steel heated to white heat, it
must be allowed to cool slowly to a lower degree than that to
which unhardened steel has to be heated to in order to con-
vert its cement-carbon into hardening-carbon."

" 4. The transformation of cement-carbon into hardening-carbon takes place quite suddenly, as soon as the requisite temperature has been reached. On the other hand, the conversion of hardening-carbon into cement-carbon takes place more gradually, and is spread over a more extended period of the heating, as well as of the cooling process."

" 5. The transformation of hardening-carbon into cement-carbon is always accompanied by a liberation of heat, and it is therefore probable (although I have not been able to verify this by observation) that the transformation of cement-carbon into hardening-carbon is effected with the expenditure of a certain amount of heat."

" 6. If hardening-carbon, in heating or cooling, is converted, completely or to its greater part, into cement-carbon, a crystallization will result quite abruptly, yielding a fracture which will prove all the more crystalline in proportion as the former texture of steel had been coarsely crystalline."

" 7. Sudden cooling will never produce an amorphous or finely crystalline fracture in a steel which, immediately before the commencement of the sudden cooling, had been coarsely crystalline, but it will prevent from being rendered crystalline a steel which, just before being suddenly cooled, had been amorphous, or in a state of liquefaction. To put it in other words, sudden cooling merely serves to fix or perpetuate the texture possessed by the steel immediately before cooling."

" 8. The transformation of hardening-carbon into cement-carbon not only necessitates a certain degree of heat, but also requires a certain amount of time; whereas, on the contrary, the transformation of cement-carbon into hardening-carbon seems to be merely dependent on the proper degree of heat. It is for this reason that sudden cooling can prevent the transformation of carbon."

" 9. The crystallization of steel requires a certain amount of time as well as a certain degree of heat." " If the duration of the cooling process is cut short by quenching in water or in some other way, the development of crystallization is partly or totally prevented."

With regard to the development of gross granulation, the same gentleman has shown that heating the steel above

the point W (*which we may assume is about* 750° C.),* the size of the granules gradually increases with the temperature, and the most coarse structure is obtained by heating to the highest temperatures, and that the structure remains coarse whether the steel is quenched suddenly or allowed to cool slowly from the point to which it has been heated. It is shown, however, that when the steel is heated to the point W, and is allowed to cool slowly to the point V (*just below* Ar_1, 620° C.),* the structure is coarser than it is if suddenly chilled from that temperature.

The experiments of Brinell were made on steel containing about a half per cent of carbon. Osmond[6] has studied, by micrographic methods, the effect of heat treatment on steels containing different contents of carbon, and says:

" I. *Steel with* 0.02 *per cent Carbon.* — It would seem that the structure of pure iron is almost independent, at least within certain limits, of the temperature of heating and the rapidity of cooling."

" II. *Steel with* 0.14 *per cent Carbon.* — In proportion as the temperature of the reheating rises, all other things being equal, the polyhedrons of ferrite enlarge, slowly at first and keeping their forms. Above 1000° they become irregular, and tend to lengthen in groups of juxtaposed bands. The pearlyte generally remains exterior to the arrangement of ferrite and stratifies in seams." (See Photograph No. 3.)

" For a given steel, the sizes and shapes of the grains are characteristic of the temperature of reheating, with a practically sufficient precision."

" III. *Steel with* 0.45 *per cent Carbon.* — According as the temperature of reheating is raised, the pearlyte forms polyhedrons more and more regular, which the ferrite envelops with a net-work more and more perfect, and in the interior of which it thrusts parallel ramifications. After heating at 1390° the metal is burnt. The polyhedrons have become so large that a photograph with the small enlargement of twenty diameters is necessary to give an idea of the whole."

" There are no metals where the temperature of reheating inscribes itself in characteristics clearer than in steels of medium hardness."

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* The words in italics are mine.

" IV. *Steel with* 1.24 *per cent Carbon.* — On heating to 1015°, the hard nucleus is burnt and divided into beautiful polyhedrons by a continuous and cellular net-work of cementite.   At 1330° the mass is altogether burnt; the polyhedrons are of great size, and frequently separated by fissures with a narrow border of ferrite, which probably arise from the introduction of oxidizing gases.   As for the remainder, the principal mass is always pearlyte, whatever the temperature of reheating may be ; only, the higher this temperature has been, the more the isolated parts of parallel layers tend to develop."

I have practically repeated all of Mr. Osmond's microscopic work given in the paper referred to, and when the conditions were rigidly adhered to, the results obtained were the same.

Granular Structure of Burnt Steel.

In studying the structure of open-hearth steel which had been burnt by a user and returned to the maker as bad (a very common condition of things, by the way), it was observed that at the parts where it had been actually burnt the growth of the granules reached a maximum, and that, exactly as described by Mr. Osmond, they then separated at many points and tended to form spherical grains.   Gases had formed or developed in the interior, which had exerted such pressure as to cause blisters or excrescences to arise from the surface, and these projected about an eighth of an inch.

Immediately below these growths the granules were very loosely held together, and a fracture of the steel was easily effected, and on the fractured surface the granules were easily studied.   They were found to be moie or less tarnished with a blue or brown film of oxide, and the examination of a polished and etched specimen clearly showed that at the junctions of some of the grains they were not united, and near the burnt surface of the bar there was found intergranular oxide of iron, which could not have been originally present.

Some of the granules were very large, measuring a quarter of an inch in diameter, and the spaces between the grains were clearly seen.   The Photograph No. 3 is an illustration of this.
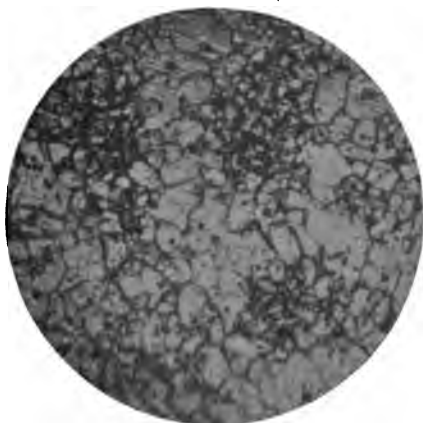
No. 2A. Wigan Saniter Soft Steel,
0.11 per cent Carbon.
Same as No. 2, after heating to 830° C. and
cooling naturally. Magnified 20 diam.
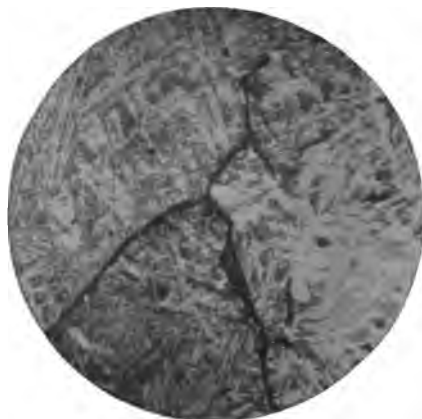
No. 3. Burnt Bulb Angle.
Showing intergranular spaces and juxta-
posed bands.
Magnified 30 diam. Etched 1 min. in iodine.

No. 4. Burnt Bulb Angle.
Same as No. 3, after heating to 900° C. for
2 minutes.
Magnified 30 diam. Etched 1 min. in
$^1|_{10}$ nitric acid.

No. 5. Saniter Decarburized Bar.
Heated for 3 hours to 700° C., showing the
commencement of coarse granulation.
Magnified 50 diam. Etched 30 min. in
$^1|_{10}$ nitric acid.

At other parts, where the heat was just short of that required to cause excretional growths or actual burning, the structure was still very coarsely granular; but on heating it up again to about 900° C., and then allowing it to cool naturally, the original fine structure was restored to it. In the burnt parts, where there was sprouting and the grains were oxidized in the interior mass, cooling and reheating to 900°, although resulting in the breaking up of the huge grains into finer grains, left the original oxidized envelopes, which retained their form. It is then easy to tell by the microscope whether or not steel has been burnt, and also if, after being burnt beyond recovery, it has been reheated again. The Photographs No. 3 and No. 4 are of the same piece before and after heating to a little above 850° C.

The mechanical tests of pieces cut from the burnt portions where the steel was covered with excrescences, and of pieces cut from the sound steel close to but not in the areas where the excrescences were noticed, are not without interest, as they show that this steel at least was not damaged until intergranular spaces were formed. The difference in the temperature between the areas could have been only a few degrees, and the structures as revealed by the microscope were practically of the same coarsely granular character, the only difference being that in the burnt steel there were intergranular spaces, whilst in the other parts they were absent. The following chemical and mechanical tests were made of this overheated and burnt bulb angle :

Chemical and Mechanical Tests of Steel Made in the Open-Hearth Furnace from Hæmatite Pig Iron, after Rolling into Bulb Angles and Heating to a Burning Temperature.

Analysis.

	Per cent.
Carbon	0.235
Manganese	0.359
Silicon	0.055
Sulphur	0.065
Phosphorus	0.063

Mechanical Tests.

The pieces tested measured 8 × 1.5 × 0.46 to 0.55 inches.

	Burnt pieces.		
	1.	2.	3.
Tensional breaking strain, tons per sq. inch	25.1	16.85	26.9
Elongation in 8 inches, per cent . . .	1.0	1.5	14.0

	Overheated, but not burnt.	
	1.	2.
Tensional breaking strain, tons per sq. inch	27.8	27.5
Elongation in 8 inches, per cent . . .	24.0	24.0

	Good part not overheated.		
	1.	2.	3.
Tensional breaking strain, tons per sq. inch	26.5	29.8	26.8
Elongation in 8 inches, per cent . . .	26.0	24.0	25.0

It will be noticed on comparing the results that heating to close upon the burning-point has apparently no injurious effect on this material.

The compound granules in the strongly heated portion were very coarse, and it appeared that although it did bear a steadily applied strain, it might snap off readily by the application of a violent percussive blow. Pieces were, therefore, tested under a steam-hammer, but in no case could a fracture be easily produced.

The structure of the large grains, as will be seen in the photograph, consisted of bands or strips of ferrite and pearlyte arranged more or less parallel to each other. It would appear, then, that such a structure, provided there is no intergranular separation, is a remarkably tough one.

Comparative trials on steels with higher percentages of carbon are being made, and when complete the results will be presented to this Institution.

Granulation of Iron and very Soft Steels at Low Temperatures.

The character of the structure in practically pure iron and soft steels is greatly influenced by the length of time such metals are heated.

Professor Arnold[7a] has shown that the elongated granules in a soft Swedish bar, produced by hammering or rolling it at a heat under redness, do not reassume the normal equi-axed granular form until heated to 750°, and concludes that 750° is the crystallizing point of iron. It would appear, how-ever, judging from what follows, that very low carbon-steel and carbonless iron will granulate at a much lower tempera-ture provided the necessary time is given.

The material on which many of my researches were made consisted of very pure iron made by the Wigan Coal and Iron Company in their open-hearth furnace by the Saniter process. This material contained a little over 0.1 per cent carbon, and in order to eliminate this, the ⅜-inch bars used were heated in iron oxides in a furnace used for the production of malleable cast iron, and were ore annealed three times over.

The analysis of the iron before and after treatment was as follows :

	Before Decarburization.	After Decarburization.
	Per cent.	Per cent.
Carbon	0.115	0.013
Manganese	0.150	0.150
Silicon	trace	trace
Sulphur	0.024	0.024
Phosphorus	0.010	0.010

The bars were tested mechanically in the same state as they left the rolls, also after decarburization, and one of the latter was heated to about 750° C., and another to whiteness in an open-hearth furnace, and they were then quenched in cold water.

Normal Bars.

	1.	2.
Tensional breaking strain, tons per sq. inch	21.26	21.58
Elongation in 2 inches, per cent . . .	53.12	53.12
Contraction of area, per cent . . ,	78.00	79.70

Decarburized Bars.

	1 A.	2 A.
Tensional breaking strain, tons per sq. inch	19.97	20.94
Elongation in 2 inches, per cent . . .	43.75	40.62
Contraction of area, per cent . . .	89.00	91.00

Decarburized Bars Heated and Quenched.

	1 A.	2 A.
	Heated to and quenched from	
	750°.	Whiteness.
Tensional breaking strain, tons per sq. inch	20.94	21.50
Elongation in 2 inches, per cent . . .	46.87	43.75
Contraction of area, per cent . . .	91.70	91.00

The test-pieces of all the decarburized bars were drawn out at the points of fracture nearly to pencil-points.

When soft iron is reduced in section by passing it cold through a steel drawplate, the original equi-axed polygonal granules of the normal iron assume a lenticular appearance in section, and the material increases in toughness and hardness. The microscope reveals no other change in the structure than a change in the form of the grains.

It is known that by heating such drawn-out and hardened material to a dull red heat its original ductility is restored. The question naturally presenting itself was whether or not such physical change is accompanied by a structural alteration. To answer this, the pencil-points of the pieces of pure decarburized soft steel just described, formed by pulling the bars asunder in a testing-machine, were sawn through their centers vertically, and these were polished and etched, and then were gently heated to various temperatures.

The first sample treated was heated for two hours to 650°. It was then removed, and after cooling it was polished and etched. The structure was found to be completely altered, the lenticular forms had entirely disappeared, and all the newly formed granules were more or less equi-axed, resembling those of ordinary iron, but with this great difference: the relative diameters of the granules varied approximately with the lesser diameters of the original lenticular grains. On actual measurement, they had the original dimensions of 0.125 mm. at the wider portion, and 0.025 mm. at the extreme point. It was difficult to determine the lengths of the grains at the narrow ends, as they had the appearance of more or less confused fibers, but there was not so much difficulty in measuring their width. After heating, most of the granules maintained the original lesser diameters, but they were on the

average of equal diameter in the other direction. Many of the larger granules were split up into many of smaller cross-section, but it did not appear that the original smaller granules had been so affected.

The second piece was heated for an hour to 625°, the melting-point of aluminium. The same change as in the last case was effected. The granules were equi-axed and graduated in diameter according to the extent of the original extension.

These results appeared to be so contradictory to those obtained by Professor Arnold,[7a] that I repeated his experiments upon two Swedish bars made by the Walloon process, which were forged at a barely dull red heat in order to elongate the granules. They were, when cold, cut up and heated in the manner described below. The first pieces were heated to 700° C. quickly, and were allowed to cool on a cold firebrick. On examination, no apparent change had been effected, thus confirming Professor Arnold's result under the same conditions. They were then reheated to the same temperature, and the heating was continued for three hours, after which they were again cooled, polished and examined. The granules were now quite altered; they were equi-axed, and, moreover, were more than twice the original diameter.

There can be no doubt that heating at 700° C. causes a reorganization in crystalline structure, and that although the heating at that temperature for a short time only does not apparently effect any change, yet there must be some slight alteration not readily detected with the microscope.

In order to still more thoroughly probe the matter, pieces of Swedish bar containing 0.11 per cent carbon were placed in different positions in the flue of a gasworks at Middlesborough. They were put in when the retorts were at full heat, so that what fluctuations in temperature there were sure to be would not rise above those at the time the samples were placed. They were left in that flue for two months, and were then withdrawn. The samples heated to just visible redness were scaled and had become coarsely granular. The temperature we may presume did not exceed 600° C.* The second

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* Aluminium and antimony, at their freezing-points (625° and 632° C. respectively), are distinctly red in diffused daylight, and are visibly red

piece was placed at the point where the red was barely visible. On examination, the granules were found to be from eight to ten times the diameter of those in the original sample before heating. The third sample was placed where lead melted but zinc would not fuse (between 326° and 419°). No change could be detected in this sample.

It might be argued that the temperatures may have occasionally risen above those given, and I am quite aware of the possibility; but as the second and third samples had not any scale on their surface after such long-continued heating, we may be certain that the temperature was very low. Nevertheless, the exact maximum temperatures given cannot be considered as beyond doubt. It would be difficult to maintain a constant heat for two months, and the flue of a gasworks constantly at work night and day appeared to be the best practical condition at command.

The following trials were also made with cut sections from the Wigan decarburized steel.

Three rondels were placed in different positions in a gas-heated muffle-furnace, the back of which had a temperature of aboot 1000°, the middle part about 800°, and the front about 700° C. The exact position where these temperatures prevailed was determined by the Le Chatelier pyrometer, and the rondels were placed at the recorded points. In five minutes the specimens had attained to the required temperature, and they were at once withdrawn and were placed on a cold brick, where they rapidly cooled down.

A portion of the same bar, half an inch round, was heated in a blacksmith's fire till it scintillated; it was then allowed to cool naturally.

Several rondels were also heated for four hours to temperatures varying from 1000° to 700°, and were withdrawn from the heat, and were allowed to cool in the air. All the specimens were polished, etched and examined, with the following results, viz.:

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on cooling for some time after they have solidified. On actual trial, I found that in a room quite dark I could see them distinctly till the temperature of 500° C. was reached, beyond which the heated object appeared quite black.

Table showing Effect on the Structure by Heating Iron to Different Temperatures.

	Diameter of Granules. Millimeters.
Iron before treatment	0.228
Rapidly heated to 1300° C., cooled out of fire . . .	0.152
do. do. 1000° C., do. do. . . .	0.152
do. do. 950° C., do. do. . . .	0.152
do. do. 800° C., do. do. . . .	0.228
do. · do. 750° C., do. do. . . .	0.228
Heated for 4 hours to 1000° C., do. do. . . .	0.110
do. 4 do. to 950° C., do. do. . . .	0.125
do. 4 do. to 800° C., do. do. . . .	0.223
do. 4 do. from 700° to 750° C., cooled out of fire .	2.520 & 0.31

One half of the last sample was much more coarsely granulated than the other.

One of the Saniter bars was forged down to a section of a quarter of an inch square, and in order to produce an initial fine grain, it was then heated to and cooled from 900° C. This bar was cut up into pieces an inch in length, and the various pieces were heated in a gas muffle-furnace for different lengths of time and to various temperatures. The heat varied somewhat, but not more than about 10°.

One piece, heated for three hours to about 730°, on cooling, polishing and etching, showed clearly enough that at different points over the face of the sample there were large isolated granules, some of them an eighth to a quarter of an inch apart. The Photograph No. 5 indicates one of these large granules completely surrounded by grains of smaller diameter. This example is most instructive, as it indicates that reorganization and crystallization start from *isolated centers*, and have a gradual growth at about 730° C.

If this conclusion is correct, then long-continued heating at that temperature should be followed by the development of huge granules. A sample heated for twelve hours to 730° at one end and 620° at the other proved this to be the case, for the granules extended the full width of the bar at the hot end to within a sixteenth of an inch of the other extremity. The polished and etched structure was very beautiful, and no magnifying was required to see the huge grains.

The same experiments were repeated on a slightly differ-

ent plan. It was thought that if comparatively long bars were used instead of small cut sections, and that if they were heated to 1000° at one end, the other ends being allowed to project out of the furnace, a graduated temperature would be obtained, and all the change-points would be clearly marked on a longitudinally cut section.

The first trial was made upon one of the bars three times ore annealed of the Wigan soft steel, which was heated at one end to 1000°, the other end to 400°, for a period of seven hours. To my astonishment, excepting above the higher point near 900° C., the original coarse structure did not show any very marked change. There was a slight development between 750° to 600°, but the granules in that portion heated to above 900° were half the original diameter.

In the second trial the bar was forged to a quarter of an inch square, and heated as in the last experiment for six hours. In this case the granules were fine to commence with, and there was a decided growth between 730° and 650°, and a breaking up or refining of the structure between 850° and 950°.

In the third trial the results were similar to the last described, but the development of the granules at 650° to 750° was very slight, although the heating has been continued for twelve hours. Pieces cut off from these bars and heated to from 650° to 750° developed very coarse granules.

It was noticed that the coarse granulation commenced to form at the surface of the bars, and in many of the results given it did not penetrate very far into the interior.

The question arises, Does iron when heated absorb oxygen, nitrogen or hydrogen gases from its environment, and if so, are they responsible in any way for the development of this peculiar crystalline granular growth?

The commencing of the growth of the granules at th surface certainly would appear to justify the opinion that they do, but it will only be after further systematic research that we shall be able to definitely come to a conclusion.

The conflicting and anomalous results referred to show what a complex study the heat treatment of iron and steel really is, and how dangerous and foolish it is to make dogmatic generalizations with our present imperfect knowledge.

The last trial was repeated on a larger scale. A bar of soft Swedish Bessemer iron, ten feet in length, was inserted from the flue end into an inclined reheating furnace, and was left there for about six weeks, and then was taken out and allowed to cool. The heat to which it had been subjected of course was graduated, and varied from about 300° at one end to about 900° at the other. When the scale was removed, it was found that at the end which had been hottest the bar was pointed, due to oxidation, and the diameter gradually increased to a point eight feet from the end where no scale had formed. Sections were cut out a foot apart, and were microscopically examined. The Diagram C shows the results.

It will be seen that the size of the grains at each end of the bar are equal, but that at a certain point it is exceedingly coarse. Presumably we may conclude that this point is where the temperature was between 730° and 600° C. No attempt could be made to actually determine it.

Steel with Various Amounts of Carbon.

Several bars about eight inches in length, and about five-eighths of an inch in diameter were bound round a porcelain tube. The ends were all in the same plane. The porcelain tube was closed at the end which had to be placed in the fire, to prevent any free passage of gases through it. The whole set was placed in a muffle-furnace which had a temperature of 1025° C. at the back. As the bars were much longer than the muffle, they projected some distance from its mouth, the result being that one end of each of them was heated to 1025°, the other ends were not visibly red. After the temperature of the muffle became constant, the thermocouple of a Le Chatelier pyrometer was inserted into the porcelain tube, and the temperature recorded at various points at equal distances apart, from the hottest to the coolest portion in the front. The heating was continued for six hours, and during the whole of that time the temperature did not vary more than 10°. All the bars were then removed, and were allowed to cool in the air naturally. When cold they

were cut up and examined after making fractures and micro-sections.

I am quite conscious that the temperatures recorded in the center of the bundle of steel bars would not truly represent the actual temperature of the bars themselves at the same points, the results therefore cannot be accepted as more than approximate. Apart, however, from the exact knowledge of the temperatures, they furnished in each bar structures developed by a graduated heating, which on longitudinal sectioning could be readily examined, and any marked change readily detected.

The diagrams on page 311 clearly show at a glance the change-points and the general character of structure with relation to that in the bars before heating. They do not give the actual size of the granules at each given temperature. This will be given in a future paper, when more extended work has been done.

The bars had the following composition :

	1. Per cent.	2. Per cent.	3. Per cent.	4. Per cent.	5. Per cent.	6. Per cent.
Carbon	0.013	0.115	0.21	0.47	0.86	1.14
Manganese	0.150	0.150	0.202	0.137	0.055	0.202
Silicon	trace	trace	0.028	0.028	0.055	0.037

It will be seen that there are two change-points in the practically carbonless iron, one at about 900°, and the other 650° to 710°.

In a bar containing 0.11 per cent carbon, which by the way was part of the same bar as the last but was not ore annealed, there was a marked change at 870° C., but no other, the granules becoming less and less until they reached the temperature of 670° C., where they were apparently the same as they had been originally.

In the bar with 0.21 per cent carbon the structure was very interesting, as it was remarkable in being far from homogeneous. The carbon was distributed in the central star-shaped area shown in the Photograph No. 22. The light parts in the photograph represent practically pure iron, and the star of dark parts where the carbon was located. It is probable that this area contained about 0.30 per cent carbon.

DIAGRAM B. — *Showing the Changes in the Relative Size of the Granules on Heating Steels for Seven Hours at between 500° and 1025° C.*
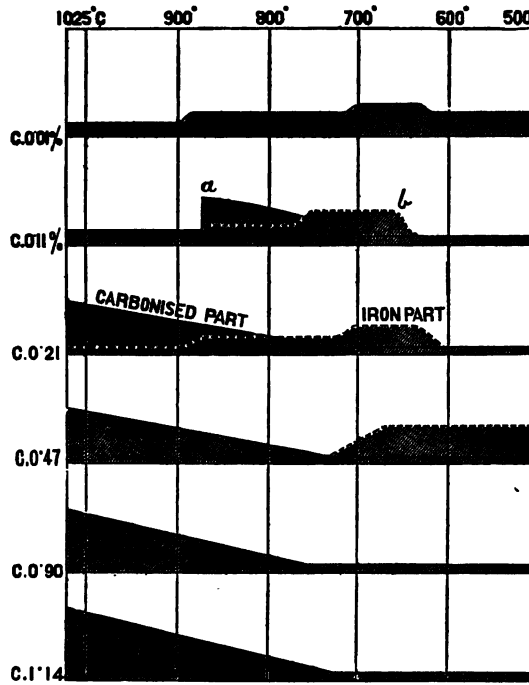
The vertical height of the shaded parts represents the relative diameter of the granules.

There were two samples of the same 0.11 per cent carbon-steel tested, *a* and *b*, the behavior of which were quite different.

The steel with 0.21 per cent carbon had a segregation of carburetted steel and free iron.

The dotted line on the right of the 0.47 per cent carbon-steel represents what takes place on heating carbon-steels of "coarse" structure according to Brinell.

DIAGRAM C.
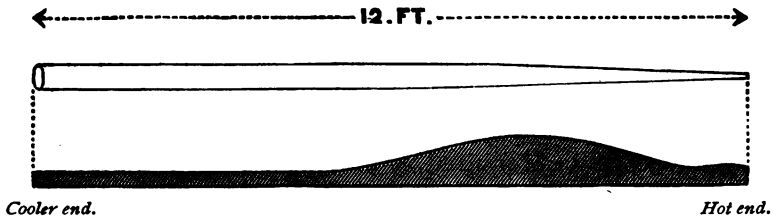
The shaded part represents the relative size of the granules.

At the end, heated to 1025°, the star had a very coarse structure, whilst the areas surrounding it, where little or no carbon was present, were fine.

At the temperature of about 750° the star was fine-grained, and continued equally fine to the cold end, the surrounding iron being coarsely granular, and this continued coarser than the central star to 600° C., beyond which the whole section appeared regular throughout in the condition it left the rolls.

It was seen that the coarseness and fineness of the two clearly defined areas, then, were reversed at the two extremes of 1025° and 600°.

The three Photographs Nos. 8, 10 and 22 are three distinct structures developed in the same bar by different heat treatment.

The steel containing 0.47 per cent had only one structural change-point, at 730°. The grain was very fine to commence with. Had it been coarse, the structural changes would have been different, according to Brinell's researches, and may be illustrated by the dotted line at the right hand of the diagram.

The steel with 0.90 per cent carbon had only one change-point, and that was at 755°. It is difficult to understand how it is that the change-point of the 0.9 per cent carbon-steel is higher than that containing 0.47 per cent. Probably the silicon is responsible.

The steel with 1.14 per cent carbon had a marked change-point at 730°. The grain in the original bar was very fine, and the cementite was broken up and was distributed in isolated strips. At the point 730° the cementite began to form, very fine meshed, round the grains, and these became more and more pronounced, and the granules larger and larger as the heat increased.

A smaller bar, a quarter of an inch square, of the same 0.11 per cent carbon, was heated for twelve hours to 900° C. at one end, while the other end projected from the furnace. The structure of this bar was very marked. It was fine grained at both ends, but in the middle, where it had been heated to between 750° and 650°, it was coarsely granular, and no microscope was required to see the clearly defined junctions between the coarse and fine structures. In this case the long heating in an oxidizing atmosphere had removed the

carbon, and thus had lowered the point where actual reorganization was effected.

In seeking to ascertain the cause of the breaking up of the coarse structure of ferrite by reheating, several pieces of the Saniter steel with 0.11 per cent carbon, after annealing in a slag ball, were heated to various temperatures and then were quenched in water. The first, heated and quenched from 700°, showed no alteration of ferrite between the areas of pearlyte. The second, heated to 750° and then quenched, on polishing *only*, left what were the pearlyte areas in bold relief, bright and hard, showing that the carbon had diffused from the laminæ of carbide to those of ferrite, but the ferrite outside these hard areas was unaffected.

On heating to, and quenching from, 830° C., the polished and etched section had a remarkable appearance. The entire surface was covered at comparatively wide intervals with dark spots. The centers of these were where the pearlyte had originally existed, but the carbon had diffused very much beyond the original boundaries. The grains in these areas were fine.

On treating a third sample by heating to 830° C., not chilling this time, but allowing to cool naturally, the structure was more easy to study as the pearlyte was redistributed between the grains, and it could be easily seen to what point the carbon had diffused. The Photograph No. 2A clearly shows that where the carbon has diffused into the ferrite its coarse structure is broken up. We conclude from these results that the breaking up of the coarse structure in carbon steels is not due only, as Brinell maintains, to the coincident change of cement to hardening carbon, but also to the carbon diffusing after such change has been effected.

In considering these results, we see that pure iron behaves in exactly the opposite way under heat treatment to what it does when associated with much carbon. At low temperature it generally becomes coarsely granular; at medium temperatures, between 750° and 860°, it is not so active; at the higher temperatures, 900°, its structure becomes fine, if it happened to be coarse at between 750° and 860°. In other words, on slowly heating up carbonless iron to between 600° and 750° C., it develops an exceedingly coarse structure; in

passing from 750° to 860° it appears to change very little, the coarse structure remains, but as soon as the heat rises above 870°, or thereabouts, it is replaced by one of fine degree.

Practical men will be ready enough to say, as they never have carbonless steels to work, the results recorded are of little value to them. The question to them is, Will the commercially supplied material in daily use develop the same kind of brittleness? In answer to that I have to say, that it was owing to having many samples of exceedingly brittle commercially supplied steel repeatedly brought under my notice from time to time which induced me to make this research, and as a matter of fact soft steel is often supplied with under 0.1 per cent carbon, and users by the processes they adopt sometimes burn out a portion of the carbon, leaving material little different from carbonless iron; and I need scarcely draw attention to the fractures in bicycle tubes and other finished products, which are often coarsely granular. In such brittle material, as a rule, the carbon has been found existing, not in areas or patches of pearlyte, but in the state of massive cementite imbedded in pure carbonless iron. In such steels, containing between 0.03 per cent and 0.08 per cent carbon, the actual approximate volume of the massive cementite containing about 7 per cent carbon is from about 0.43 per cent to 1.1 per cent of the whole mass, and as it is so completely isolated from the iron, the latter then evidently must be free at comparatively low temperatures to develop coarse crystalline granules.

One of the instances just referred to of excessively coarse granulation in very soft steel was thoroughly examined. It contained —

		Per cent.
Carbon	. . . .	0.040
Manganese	. . . .	0.275
Silicon	. . . .	0.053
Sulphur	. . . .	0.025
Phosphorus	. . . .	0.035

Judged from the analysis, there was nothing to indicate inferior material, but the bar was returned to the steelmaker as rotten, and as a matter of fact it was so brittle that, although about one inch by one inch in section it could be easily

No. 6.　Swedish Bessemer Steel,
0.04 per cent Carbon.
Coarsely granular.
Magnified 2 diam.　Etched 1 min. in
$^1|_{10}$ nitric acid.
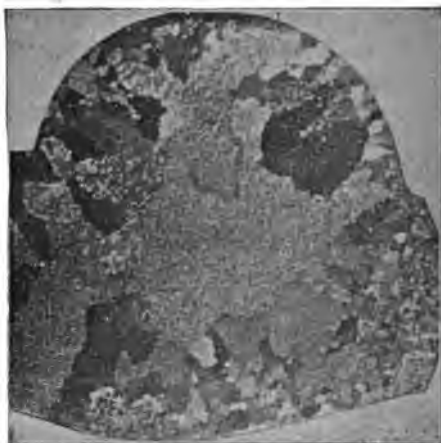
No. 7.　Swedish Bessemer Steel,
0.04 per cent Carbon.
Coarsely granular.
Magnified 3 diam.　Etched 1 min. in
$^1|_{10}$ nitric acid.

No. 8.　Steel.
Same as No. 10, after heating to 900° C.
and cooling naturally.
Magnified 3½ diam.　Etched 1 min. in
$^1|_{10}$ nitric acid.

No. 9.　Swedish Bessemer Steel.
Inside of No. 6, showing massive cementite.
Magnified 300 diam.　Etched 1 min. in
$^1|_{10}$ nitric acid.

broken up, yielding a coarsely granular fracture over all the surface, with the exception of about a quarter of an inch in the center, and some of the grains measured a quarter of an inch across their faces. It was clear that from some cause this granulation had been developed by treatment after it had been rolled and delivered to the user. Had he subjected it to the very simple test of heating it up to a bright-red heat and then allowed it to cool naturally in the air, he would have found that it would have become tough and finely granular. This test was applied in my laboratory, and the result is illustrated by the Photographs Nos. 6, 7 and 8.

Photographs Nos. 6 and 7 are of polished sections of the bar in its brittle condition, magnified only two diameters. No. 8 gives the character of the structure after heating up to 900° for one minute, and allowing to cool in the air.

On carefully examining the section under high power, it was observed that the carbon was entirely in the state of massive cementite laid between the larger grains at their junctions, and in isolated masses in the center of the bar where the granules were very fine. Photograph No. 9 illustrates this.

We are satisfied that this was rendered brittle by heating it for a long time in either an annealing furnace or an ordinary heating furnace at a low temperature. Possibly the bar had been left all night in the reheating furnace, and was removed next morning before heating it up again. The segregated cementite affords proof that it was very slowly cooled between 700° and 600° C.

Considering that 0.04 per cent carbon was present in this material, and that it could be most easily seen, under the microscope, distributed at wide intervals all over the face of the section, it shows conclusively how delicate a test the microscope really is for the detection of minute quantities of carbon in annealed material. It also shows that it must be almost, if not all, separated as carbide, and that little or none can be left in the state of a solidified solution in the surrounding iron.

Columnar Granular Structure.

Granulation of a peculiar kind, first noticed by Dr. Percy, although not studied by him, is that which may be called "columnar granulation."

I quoted Dr. Percy's remarks in the introduction, and laid special stress on the fact recorded, that the bar having columnar crystals was covered with oxide of iron. Dr. Percy does not give any analysis of the iron, but, as will be presently shown, it probably contained some carbon.

During my investigations ([18a]) on malleable cast iron it was found that the exterior layer of every partly decarburized malleable casting consisted of decarburized iron, varying in thickness according to the amount of carbon left in the center, and the granulation was arranged in this layer on quite a different system to that usually found in iron; instead of the irregular shapes and polygonal forms referred to previously, they were arranged in columns which radiated from the exterior inwards, and terminated at the point where there was carbon.

If the temperature in the annealing furnace is not fluctuating, it is possible on annealing steel bars, with about 0.21 per cent carbon, at a temperature between 700° and 800°, to obtain long columns or grains which pass from the surface to the center.

The Photograph No. 10 is a perfect illustration of this. It originally contained 0.21 per cent carbon, but after annealing at about 750° C. for three weeks in lime it contained only a trace. Photograph No. 11 is that of a steel treated in the same way as the last, but it originally contained 0.47 per cent carbon. The central dark area contains about 0.3 per cent carbon; the areas surrounding it only traces.

When these samples were heated to 900° C. and were quenched in water, the columnar structures disappeared, and were replaced by the ordinary granular form. The Photograph No. 8 equally illustrates the change in No. 10 as in Nos. 6 and 7.

It will be noticed on comparing No. 11 *a* and *b*, that the dark central area where the carbon exists is of greater diameter in the steel after heating and sudden quenching than it

No. 10. Steel Annealed in Lime at about
700° C., all the Carbon (0.21 %) removed
and columnar structure produced.
Magnified 3½ diam. Etched 2 min. in
¹|₁₀ nitric acid.

No. 11. *a.* Steel Annealed in Lime at about
750° C., Carbon originally 0.50 per cent.
b. Same steel heated to 900° C. and
quenched in water.
Magnified 3½ diam. Etched 1 min. in
¹|₁₀ nitric acid.
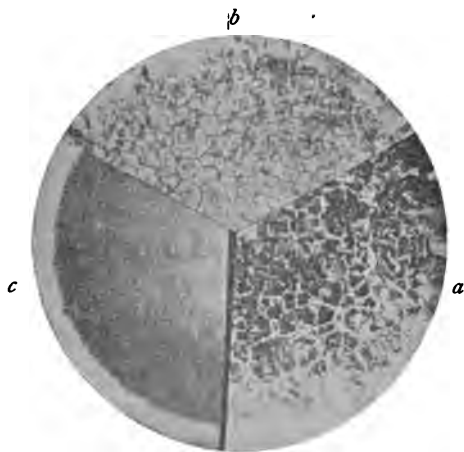
No. 12. *a.* Steel 1.40 per cent Carbon,
Annealed in Ore.
b. Same steel heated to 800° and quenched.
c. Same steel heated to 900° and quenched.
Magnified 6 diam. Etched 1 min. in
¹|₁₀ nitric acid.

No. 13. Part of a Grain of Pure Iron.
Showing square crystals and lamination.
Magnified 250 diam. Etched 3 min. in
¹|₁₀ nitric acid.

was in the annealing material. This is a very excellent illustration of the fact so clearly shown by Mr. Osmond, that on heating steel the carbon apparently expands like a gas, and diffuses or combines with the surrounding iron.

Although it is difficult to decide with certainty the causes resulting in the development of these radial columns, there can be no doubt whatever that they are related in some way with the coincident passage of the carbon from the steel, for the following reasons :

1. Carbonless iron has not in my research been made to assume the columnar structure by any simple heat treatment.

2. If the annealing is done in a non-oxodizing atmosphere or environment, the peculiar structure is not developed.

3. It is not effected by the diffusion of carbon from one high-carbon steel to a pure iron when they are brought in perfect contact and annealed together.

4. It is only developed when the carbon is removed by oxidizing agents from the surface, when the temperature is below 850° C.

When a round piece of steel containing 1.4 per cent carbon, $\frac{3}{8}$ inch in diameter, is annealed for a sufficient length of time, so as to produce a ring or outer circular layer of two hundredths of an inch in thickness of carbonless iron, no amount of heating followed by sudden quenching will induce the carbon to remain in this ring or layer, although we know that in the process of heating the steel to about 900° carbon must pass into it. The composite Photograph No. 12 proves this. It represents the same bar annealed and then heated to 800° and 900° C. respectively, and suddenly quenched in cold water, and then etched with nitric acid. It shows most clearly that the carbon, on heating, has diffused to a fixed line, and then has been abruptly arrested. The width of the rings in the annealed and quenched steels was 0.12 mm. in the former and 0.090 mm. in the latter.

There is no other solution to these phenomena than the acceptance of the fact that there is a diffusion of oxidizing gases from without into the metal, and a diffusion of carbon outwards from the center, and that the point where the carbon area ends is the point at which the entering oxidizing gases are saturated with the outwardly diffusing carbon, the carbon

being completely oxidized as rapidly as it diffuses beyond this clearly defined boundary.

It follows from this that in proportion as the carbon is more and more distant from the surface and is limited as to the distance it is capable of traveling, the diffusion of the oxidizing gases from the surface must penetrate to a greater and still greater distance into the steel before they are saturated with carbon, and therefore the ring of external iron, free from carbon, will be correspondingly increased in thickness. This is proved to be the case, as will be seen by the Photograph No. 11.

Graham[14] has shown and proved that iron when heated to redness in a vacuum gives off a large quantity of gas, and that this contained 13 per cent of carbon dioxide, the remainder being essentially carbon monoxide. He also proved that the same iron after exhaustion, when heated in carbon monoxide, absorbed as much as twenty volumes of the gas per unit volume of iron. He does not appear to have made any trials to ascertain if mixtures of the two carbon oxides were also absorbed, but, judging from the fact that mixtures of these were given off on heating iron in a vacuum, it may be accepted as a fact that they do penetrate, and are retained in iron.

In order to determine the character of the gases which, although penetrating the steel, are incapable of oxidizing the iron, but undoubtedly oxidize the carbon, an experiment was made in which a slow current of carbon dioxide and carbon monoxide in equal volumes were passed over pure iron drillings heated to 1000° C. in a porcelain tube ; the gases leaving the tube after having become inert by their action on the large excess of iron were analyzed, with the following results :

	Per cent.
Carbon monoxide	64
Carbon dioxide	36

After a considerable volume of this mixture had been collected it was passed over powdered white Swedish raw iron. The gases, after passing over the metal heated to 1000° C., were collected and analyzed, with the following results :

	Per cent.
Carbon monoxide	97
Carbon dioxide	3

It will be seen that there is a marked reduction in the carbon dioxide in the mixture after passing over the carburetted iron.

Although there can be little doubt that it is to carbon dioxide we must attribute the main effect in oxidizing the carbon, we are conscious that any active oxidizing agent such as air, steam or oxides, capable of readily parting with their oxygen, must be the primary source of the oxygen; but it appears that they are only the means by which the carbon dioxide and carbon monoxide are produced, and it is the carbon dioxide which is directly responsible for the oxidation and removal of the carbon.

As a proof of this, if white cast iron is carefully covered with asbestos sheet, and is annealed in ore, decarburization is effected almost as perfectly as if the metal had been bedded in contact with the ore. It is possible even to decarburize steel by bedding it in granulated coke, contained in a porous case, when the case and contents are heated in ore at between 750° and 850° C. for a sufficient length of time. At a much higher temperature than this no decarburization, of course, follows, and if the temperature is raised to 1300° C. the coke parts with some of its carbon to the steel.

Judging from these facts, it would appear that the persistent and well-defined ring of iron is maintained by the diffusion from the surface not of free oxide of iron, but of a gaseous mixture having most probably the composition at 1000° C. of 100 of carbon monoxide to 50 of carbon dioxide; but this must vary greatly with the temperature, the higher the temperature the less carbon dioxide, and the greater proportion of carbon monoxide.[16]

According to Sir Lowthian Bell, the points of equilibrium of metallic iron, carbonic acid, and carbonic oxide at different temperatures are as follows:

	Carbonic Acid per 100 of Carbonic Oxide.
Low red heat	150 volumes
Full red heat	47 do.
Approaching whiteness	11 do.

It will be clear that it is only a mixture of the two gases, quite inert on iron itself, which it is possible can penetrate

below the skin of the steel or metal heated, for any excess of carbonic acid must suffer reduction to carbonic oxide at the surface immediately it comes in contact with the iron, the result being of course iron scale or oxide, and the establishment of the inert mixtures referred to. It will be seen, then, that the results of Sir Lowthian Bell give us a good idea as to what the compositions of the gases probably are, which diffuse or penetrate into solid iron at different temperatures.

When all the carbon has been eliminated, leaving a columnar structure, and when this structure is destroyed by heating to above 870°, no heat treatment I have applied ever restored it. (See Photographs Nos. 8 and 10.)

In concluding this section, it is important to note that, with the pure carbonless material I have experimented with, in no case was the coarse granular structure, produced by long heating at low temperatures, as brittle as one would naturally expect it would be, and this I conclude may be accounted for, first, because of the purity of the samples, and, second, by assuming that the crystal axes had in contiguous grains their cleavage planes heterogeneously arranged. This will be better understood on studying the crystalline structure of iron in the following section.

On close annealing for forty-eight hours pieces of tin-plate bar, in most cases the external envelopes were coarse and the interiors most finely granular. On sudden shock some of them broke off short, and others, after bending in one direction, broke on straightening. When the outer coarsely granular envelopes were planed off, the interior fine structured steel was tough, and in every way perfectly safe material. It is clear, then, that commercially supplied soft steel may be rendered unsafe by the presence of an envelope of coarse structure. In certain processes to which wire manufacturers subject their steel this peculiar envelope is produced, and it is not an unusual thing to come across brittle wire rods in which the microscope clearly proves the presence of a ring of carbonless iron, the granules of which are arranged in columnar form. All such samples, however, become tough and good on heating for a minute or two to 900° C.

It is scarcely necessary to point out to practical men the danger there must be of using material enveloped with a

coarsely granular ring, and this ring is often produced in annealing all classes of steel. It will also be equally clear that the safest way to anneal dead soft steel, if of coarse structure, is to heat it to 900° for a short time, and cool rapidly to 630°, and then cool slowly, but on no account " stew " it at between 750° and 650°; if, however, the structure is fine to commence with, long heat at 630° should be sufficient to remove all mechanical strains.

Crystalline Structure.

I have made it my careful study for three years to develop the angles of crystals in iron and steel, so that their true form could be ascertained, and I think with a fair amount of success. Naturally the aim was to obtain masses of iron as coarsely granular as possible, so as to have sufficiently large areas to enable one to examine them without the necessity of using very high power magnification ; it was, therefore, considered advisable to confine the research to annealed material, and, as was expected, it was found unnecessary, as a rule, to employ a higher power than 200 diameters.

A material readily obtainable for studying the structure of pure iron is to be found in the nodules of pure iron embedded in the solidified masses of basic slag from the basic Bessemer process. Many of these contain 99.9 per cent of iron, and they are practically free from phosphorus, silicon and carbon, and, moreover, are very coarsely granular.

Specimens of these were sawn and carefully polished, and were then immersed in nitric acid until the surfaces were very strongly corroded. The usual method adopted for the development of the boundaries of the grains, in which weak etching fluids are used and allowed to act for a short time only, was found to be of little or no value, for it is evident that unless the original surfaces were completely removed and the virgin metal exposed, uncut by mechanical means, it would be impossible to obtain the terminal angles of the crystals. The acid used consisted of solutions of nitric acid of 1.42 specific gravity and water in various proportions, from 1 part acid and 99 parts water, to 20 parts acid and 80 parts of

water, and the specimens were treated first with the weaker solutions, and afterwards with those more highly acidulated for periods varying from one minute to two or three hours. No definite rule can be laid down for etching, as every specimen appears to require its own special treatment for the most perfect development of its structure; but generally a 10 per cent acid solution gives the best results.

The results obtained are shown in Photographs Nos. 13 to 19.*

No. 13 is part of a single grain, in which the layers or plates dip at an angle. In this photograph it will be seen that the ends of the projecting layers are not symmetrical terminations of crystals, as the true angles or edges have been dissolved away when they projected above the surface.

Mr. Thomas Andrews,[5] in a paper on " Micro-Metallography of Iron," gives some interesting results obtained by the examination of sections of iron cooled in large masses, and concludes that under such conditions of treatment there are developed what he calls " primary," " secondary " and " tertiary " crystals. Judging, however, from the drawings, it would appear that what he calls primary and secondary crystals are what I call grains, and that the cubic crystals noticed (which are called crystals of a tertiary system) represent the true crystals of iron.

I believe that Mr. Andrews was the first to develop the cubic crystals of iron by micrographic methods.

It is not in all the grains in masses of pure iron that these square forms can be developed; and the most remarkable point is that frequently in the whole areas of the sections of large granules only a few crystals can be isolated on the ground mass, as is illustrated in Photograph No. 13, where a large square plate stands out on a level plain with the laminæ on the right clearly shown.

It is difficult to understand why the acid should behave in this very peculiar way, acting selectively, dissolving away certain parts more rapidly than others, when, so far as we know, the whole mass is homogeneous and of equal composi-

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* Mr. Osmond in his most recent work gives a micrographic plate of cubic crystals developed in a soft cast steel ingot.

tion throughout.   Several hypotheses of course present them-
selves as possible solutions of the difficulty ; but these I need
not trouble you with, as experimental proof is deficient to
justify their advancement.

The large square forms developed are built up of smaller
crystals of the same shape and orientation easily seen under
the microscope.   This does not of course indicate a secondary
crystalline formation.   Every crystal must be built up of an
incalculable number of molecular crystals, and the acid in
etching causes them to be separated in symmetrical masses of
greater or less magnitude.

In the process of etching, when the specimen of steel is
periodically examined as development progresses, it is found
that in the grains, where what appear to be laminæ are strati-
fied horizontally, there are formed at first excessively small
square cavities only visible under a very high power, but
later, after the continued action of the acid, these square
forms are found to be much larger, and have evidently become
so by the gradual solution of the walls which enclosed the
square space eaten out by the acid.   After a considerable por-
tion is exposed of the face or bed on which the metal dissolved
away originally rested, it begins to be attacked, and small
square cavities are formed, and these (although I have not
followed them) probably grow larger and larger as the etch-
ing progresses.   As a rule, the crystalline square forms are
the result of their solution, but in many cases the ground
mass is dissolved away in the first instance, leaving the crys-
tals in relief.

In the endeavor to find out what element in combination
with iron favors the formation of crystals capable of develop-
ment by the etching process, alloys or combinations of iron
with aluminium, chromium, carbon, manganese, silicon, phos-
phorus and tungsten, were most carefully annealed by heat-
ing to 1000° C., and were allowed to cool down to 500° in
thirty-six hours.

The combinations of iron with phosphorus and with
aluminium developed well-defined square crystals.   The com-
pounds of iron and silicon were, however, found to furnish the
most perfect material for the developing of the crystalline
structure by etching.
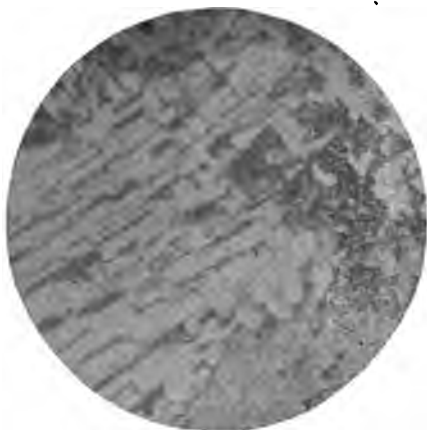
No. 16.   Silicon Steel,
4 per cent Silicon, 0.02 per cent Carbon.
Magnified 130 diam.   Etched 3 hours in
$^1|_{10}$ nitric acid.

No. 17.   Silicon Steel,
4 per cent Silicon, 0.02 per cent Carbon.
Magnified 130 diam.   Etched 3 hours in
$^1|_{10}$ nitric acid.

No. 18. Silicon Steel, $4\frac{1}{2}$ per cent Silicon.
Part of a single grain.
Magnified 130 diam.   Etched 3 hours in $^1|_{10}$ nitric acid.

The carbonless compounds with from 0.1 to 0.5 per cent silicon did not give very different results from pure iron, but when the proportion of silicon approached 4 per cent a very splendid development of crystals was obtained. The polished surfaces were etched with a solution of 10 per cent acid and 90 per cent water for from ten minutes to three hours. The joints of the grains were rapidly developed, whilst more slowly the surfaces of the grains themselves were resolved into more or less perfectly developed crystals. These in the 4 per cent silicon compound invariably assumed the form of thin square plates not more than 0.01 mm. in thickness. These plates in any single grain were stratified in the same phase and at the same angle throughout its mass, but in widely different phases or angles in adjoining grains.

The crystals developed in the compound containing 4½ per cent of silicon appeared to consist of thicker plates.

The Photograph No. 14 (Frontispiece) represents an area in the metal containing 4 per cent silicon, slightly etched.

Photograph No. 15 (Frontispiece) is the same area etched for two hours.

Photograph No. 16 is of part of a grain the tabular crystals of which dip at a slight angle to the surface, and has the appearance of the overlapping of diagonally placed slates on the roof of a building.

Photograph No. 17 represents the junction of several grains illustrating the variable dip or direction of the crystals in contiguous grains.

Photograph No. 18 represents part of a grain of a steel kindly supplied by Mr. R. A. Hadfield, containing 4½ per cent of silicon, which I believe is the most perfect crystalline structure ever developed by metallographic methods.

These carbonless silicon steels* were peculiar in the re-

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* The question might be asked, whether a carbonless compound of iron may properly be called "steel." While there still exists some difference of opinion about what should and what should not be called steel, yet all the definitions which have ever been formulated describe steel as being a compound of iron and carbon.

Carburetted compounds of iron, which, were it not for the presence of a relatively large amount of a third constituent, would in no way

spect that heating up to even 1100° C. effected no structural
change. The granular junctions remained exactly as they
were before heating, as was demonstrated by heating forged
specimens in which the granules were lenticular in form.
Heating did not restore the equi-axed granules as it does to
the drawn-out granules of ordinary steel and iron.

Mr. F. Osmond and Professor Arnold have shown that
there is no arrest-point or allotropic change at Ar_3 (850° to
870° C.) in high silicon steels and aluminium alloys. This is
coincident with the absence of structural change by heating
to above 870° C. At 700° these samples cease to be more than
feebly attracted by a magnet. We may, therefore, conclude
that at this point there is an allotropic change but not any
crystalline alteration, for, as before stated, no structural
change is effected by heating to this temperature. As carbon
is practically absent there is no arrest at Ar_1.

Even if carbide of iron was present with this high amount
of silicon, it could not decompose and absorb the heat neces-
sary to give the arrest Ar_1.

A portion of Mr. Hadfield's sample with $4\frac{1}{2}$ per cent sili-
con, together with pieces of ordinary iron and steel, were sub-
jected to the cementation process, but although all the other
samples became highly carburized, the silicon material did
not absorb any carbon whatever. This of course was naturally
to be anticipated, for $4\frac{1}{2}$ per cent silicon leaves no iron free to
combine with carbon at the temperature of the cementation
furnace.

Professor Roberts-Austen has been kind enough to deter-
mine for me the cooling curve of the steel containing 4 per
cent silicon, which proves there is only one critical point, at
703° C., and that is where the magnetic properties change,
viz., Ar_2. My own results exactly confirm those obtained by
Professor Roberts-Austen.

Aluminium in quantity, say 10 per cent alloyed with 90
per cent iron, has a similar effect in eliminating both the Ar_1
and Ar_3 points, but I have failed to obtain such perfectly

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differ from ordinary steel, may quite correctly be called nickel-steel,
manganese-steel, etc., but the extension of such terms to carbonless iron
alloys seems hardly desirable or indeed justified. — ED.

crystalline development as with the silicon steel.   The composition of the steel examined was as follows :

	Per cent.
Iron	87.700
Aluminium	10.300
Combined carbon	1.010
Graphite	nil
Silicon	0.560
Manganese	0.320
Sulphur	0.005
Phosphorus	0.019
Copper	0.065

This steel would not harden, and heating to 1200° and quenching did not alter the structure.   Neither the granulation nor the cementite were altered in the least by such treatment.

The specimen of brittle soft steel described on page 314 presented a most valuable field for examining the properties and structure of crystalline masses of nearly pure iron. (Photographs Nos. 6 and 7.)   Each separate granule could be examined and tested.   In some of them square plates were easily developed, and in one grain the peculiar structure shown in Photograph No. 19, in which plates or trains of crystals differently oriented cut through the body of the grain and also cut each other, forming angles of 60° at the intersecting points.

This remarkable sample, as I have previously observed, contained the carbon in the form of massive cementite, white, hard and brittle, which formed junctional bands between the larger granules. (Photograph No. 9.)

At first sight it would strike any one that these brittle, hard bands of carbide of iron were the real cause of the brittleness.   This hypothesis was soon disposed of, however, by testing a polished and etched section mechanically by means of the device[18b] described in a previous paper.   The lines of greatest weakness were found to be through the crystalline grains in two directions, one at right angles to the other. Photograph No. 20 represents the rectangular fracture in the middle of one of the grains.

It was not in all the grains that a fracture could be effected, but only in such where the natural cleavages of the

No. 19.   Pure Iron.
Part of a single grain, showing triangularly
arranged trains of crystals.
Magnified 100 diam.   Etched 2 min. in
$\frac{1}{10}$ nitric acid.

No. 20.   Pure Iron.
Part of a single grain, mechanically broken,
showing fractures at about 90°.
Magnified 50 diam.

No. 21.   Cubical Forms detached from a
Large Granule of Phosphoretic Iron.
Magnified 5 diam.   Not etched.

No. 22.   Steel, with 0.21 per cent Carbon,
heated 6 hours to 700° C.
Carbon concentrated in dark areas.
Magnified 3 diam.

crystals approximated to a right angle with the surface, and in a line with the direction in which the percussive force was applied.

In this specimen the granular structure was so coarse over the greater part of the external area of the section that it is not surprising that it was so extremely fragile, one single granule splitting, of course, being the starting-point for the fracture to run through the bar.

I was inclined to believe that the lines of weakness were between the granules, but it is clear that the junctions are a safeguard, and the more junctions there are the more reliable will the steel be.

I have frequently met with very slowly cooled grossly granular phosphoretic iron, and in one instance the mass of some of the granules was so great that with care they could be readily split up by properly directed force into rectangular and cubical masses. The Photograph No. 21 represents several of these. The angles are almost perfect at 90°. The amount of phosphorus was 0.75 per cent, and no carbon was present. The fracture of this specimen followed the direction of the cleavage and at the granular junctions.

In consideration of the ease with which the cleavage was effected, it would lead us to believe that phosphorus causes steel to be brittle by reducing both the intergranular[7] and the intercrystalline cohesion.

In pursuing the practice of mechanically tracing the seat of weakness in steels, I have proved in certain other cases where the granulation was sufficiently coarse to experiment upon, that although the bars tested might stand excellent tensional and bending tests, a blow suddenly applied to the center of a small section will effect a rectangular fracture through some of the grains, but that the fractures do not extend beyond the junctions of the grains in which they formed unless the contiguous grains are built up of crystals of closely approximate orientation.

Crystallization in Annealed Sheets.

From time to time I have had to analyze samples of soft steel sheets which had been returned to the makers as bad steel, but analysis rarely gave any clue to the cause of the brittleness. These samples and very many others have been most carefully microscopically examined.

Microsections polished and slightly etched of annealed brittle steel were compared side by side with the similarly annealed non-brittle material, and at first sight no difference could be detected. The size of the granules was almost equal in all, and the carbon in each had segregated as massive carbide of iron. On testing the polished and etched sections by the mechanical device before referred to, it was noticed that fracture was effected through the grains, and that cleavages through contiguous grains were nearly all in the same line or direction. This appeared to be strong evidence that the brittleness was due to the symmetrical orientation of the crystals in contiguous granules. Every sample showing this peculiarity was brittle, and each was restored to a tough condition by simply heating for a short time to 900° C. The general orientation of the crystals in the granules after heating was proved to be rearranged in multi-angular position.

On consideration, it became evident that if the crystalline structure was symmetrical and the system of crystallization cubical, cleavage should be more readily effected in such material as plates or sheets in two directions, one at right angles to the other. On experimenting with a sheet about an eighth of an inch in thickness by placing a small piece over a dished metal block and applying a sudden blow to the center, fracture was effected in the manner anticipated, in two directions at right angles to each other. The Photograph No. 23 illustrates this.

On examining a fractured surface by allowing light to fall on it obliquely, it was found that the angle at which the greatest amount of light was reflected was the same as the angle of incidence. (See Diagram A.)

One other peculiarity in the rectangularly brittle material was that in every case the lines of weakness were at an angle

No. 23. Brittle Plate broken at right angles, through cleavages of crystals. · Natural size.

No. 24. Photograph of Brittle Plate, 0.40 per cent Carbon.

No. 25. Crystallized Fe_3C. Magnified 150 diam.

No. 26. Surface of Annealed Sheet. Coarsely granulated. Natural size. Etched 5 min. in nitric acid.

of 45° to the direction in which the steel had been rolled ; and although fracture could be readily effected at these lines of weakness or cleavage, the steel could be bent over and hammered close without fracture when the bending stress was applied at an angle of 45° to these lines of weakness. Photograph No. 24 illustrates this.

Another kind of brittleness having the character of cast iron was also examined in rolled annealed sheets. In this material the fracture did not follow any special direction, as it broke up exactly like thin plates of cast iron. The weakness here was found to be principally *inter-granular*, and was quite distinct from the previously described rectangularly brittle material in which the weakness was *inter-crystalline*.

During the last two years repeated experiments have been made to produce at will the two classes of brittle steel, but hitherto without success ; but during the research much interesting information has been obtained. I am greatly indebted to Mr. W. R. Lysaght of Wolverhampton, for the assistance he has given in the research, and for permission to lay before you the following notes :

First, That it is only about 1 per cent in 10 to 18 gauge sheets in which the brittleness is observed.

Second, That in sheets between 22 to 30 gauge it has never been observed.

Third, That all good sheets from 10 to 18 gauge, after annealing, if hammered at a black heat (400° to 500° C.) and then allowed to cool, develop this peculiar rectangular or cast-iron weakness.

Fourth, That the carbon is usually very low, varying between 0.03 and 0.06 per cent in the plates which break with the rectangular fracture ; but the greater quantity of good non-brittle sheets are low in carbon, varying between 0.06 and 0.09 per cent.

Fifth, That on close reannealing rectangularly weak plates for 48 hours, they sometimes become tough and good, but not always ; and in one case a plate after reannealing for 144 hours still retained its brittle character.

Sixth, That *some* of these brittle sheets, if heated to 900° C. and made tough and good, on rerolling at the usual temperature of about 600° C. become brittle again in lines 45° to

the direction of rolling ; but as a rule rerolling such restored material does not develop brittleness.

Seventh, In some plates the brittleness is like that of cast iron, the fracture not taking any definite direction. The microscope proved that the weakness in each case is principally inter-granular, not inter-crystalline, and this material is also restored to toughness by heating to 900° C. Such plates are sometimes high in carbon, 0.15 to 0.16 per cent ; but one sample contained 0.03 per cent, and another 0.06 per cent.

Eighth, That originally good sound annealed plates, which are used as templates, and are placed on the hot-rolled sheets as they leave the rolls and are subjected to rough usage, invariably develop the rectangular weakness, and always at the same characteristic angles.

Ninth, That a plate, after it has been pickled, on heating for a few seconds to about 430° C. in passing it through the zinc bath, and then cooling suddenly in water, tends to accentuate a cast-iron weakness.

Tenth, That pickling sheets even for many hours will not necessarily produce the cast-iron brittleness.

Eleventh, That we have tried to produce it, but without success, by rolling at temperature varying from 900° to 40° C.

Twelfth, That although thousands of samples have been tested, none have been discovered with the rectangular weakness in sheets *that had not been annealed* after they left the rolls.

Thirteenth, That long roasting the tinplate bars previous to rolling into sheets does not cause brittleness in the rolled sheets.

Fourteenth, That occasionally annealed sheets are met with showing extraordinary granular development, the grains measuring $\frac{1}{2}$ to 1 inch in diameter, and in such material the weakness is inter-crystalline. (See Photograph No. 26.)

Fifteenth, That in order to detect the brittle plates in the course of manufacture before they leave the works, the cuttings from each sheet rolled are now tested.

Crystalline Structure of Cementite.

Professor Martens has shown that the cementite in spie-geleisen crystallizes in the hexagonal system, and the massive cementite in chrome pig iron certainly is crystallized in that system.

Quite recently Mr. Saniter sent to me a sample of slowly cooled, partially purified pig iron, and this gives very characteristic rhombohedral crystals, and as manganese was practically absent we may assume that it was Fe_3C, and not a ternary compound.

Crystalline Structure of Hardened Steel.

Mr. Osmond has very thoroughly studied the etched structure of hardened steels, and he apparently accepts without hesitation the authority of Mr. Michel Lévy that martensite characterized by fibers crossing each other and forming triangular figures indicate crystallites of the cubic system; but considering that rhombohedral crystals will equally give triangular figures, and that the martensite developed in Hadfield's manganese-steel, and also in chrome-steel, give figures more closely related to the rhombohedrons than to the cubes, I am inclined to doubt whether the martensite consists of crystallites of the cubic system. (See 16, Rosenbusch's *Rock-Making Minerals*, Idding's translation, Plate XV. 5, and XX.) If the structure is proved to be that of the rhombohedral and not of the cube, it would rather strengthen the allotropic hypothesis as regards hardened steel.

The whole question, however, requires to be more fully studied before we can come to any certain conclusion, and except making this note I shall not discuss it further here.

Summary.

In brief we may summarize the results of what has been stated.

First, That granules and crystals should not in future be confused together, for although a granule is built up of crys-

tals, its external form is not of any kind of crystal, as it takes its shape from its surroundings. It might be called, according to Rosenbusch, an "allotrimorphic" crystal, but the more simple term of "crystalline grain," or still more concise "grain," will be a more acceptable term to the sturdy sons of Vulcan.

Second, That grains formed in the solidification of liquid metals are large or small according to whether the freezing is rapid or slow, and they take their form from their surroundings, and this is most irregular, owing to mutual interference.

Third, That in practically carbonless pure irons and steels of fine grain produced by either forging or certain heat treatment, the grains increase in size slowly at 500° C., and more rapidly at between 600° and 750° C., and it is possible by heating at about 700° for a few hours to develop granular masses of exceeding coarseness. The cause of this appears to be due to the molecular activity, and the natural disposition for the crystals in contiguous grains to assume the same phase or axal relation with each other, and when this is brought about the boundaries or granular junctions between them cease to exist. When pure iron made coarsely granular by long heating at a dull red heat is heated between 750° and 870°, as a rule the structure is not altered to any material extent, but as soon as the temperature rises to about 900° C., the granules again become small, and heating to 1200° C. does not apparently produce any difference in their dimensions.

Fourth, That the granules in carbon-steels containing from 0.20 per cent to 1.20 per cent carbon, so far as I have been able to ascertain, do not grow in size by long-continued heating at 700° C., but that they increase in size slowly at first and then more rapidly with each increment of temperature above 750° C., the change-point varying with the carbon. This change is evidently caused by the carbon present. When, however, the coarsely granulated steel is reheated again to a little above 700° to 750° C., the coarse structure vanishes, a molecular revolution is effected, and the granules become very fine. I do not at present pretend to understand what causes this change, but there can be no doubt that car-

bon is the primary cause ; a secondary cause most probably is allotropy.

Fifth, That in steels with 0.10 to 0.15 per cent carbon containing the pearlyte in widely separated areas (a condition of things readily bróught about by annealing it in a bogie of fluid blast-furnace slag, and allowing it to cool down with it), on heating and quenching from about 750° the large ferrite grains are not broken up, and the carbon apparently does not expand or diffuse beyond the original areas, as has been previously demonstrated by both Mr. Osmond and Professor Arnold ; yet when the heating is raised to near 850°, and the steel is allowed to cool down naturally, the carbon areas are found far beyond their original positions, and exist in a number of smaller segregations, and in the whole areas where the carbon has diffused the ferrite is found existing in small grains, the grains of ferrite beyond, into which the carbon had not diffused, not being broken up. This clearly shows that it is not only the change from cement to hardening carbon, as is maintained by Brinell, which is responsible for the breaking up of the structure, but also to the diffusion of the carbon after the change has been effected.

Sixth, That good open-hearth steel with 0.23 per cent carbon may be heated to close upon its burning-point without becoming brittle, and that it only becomes truly burnt when inter-granular separation is effected, and this condition of things can generally be detected by the slight excrescences on the surface of the steel, and by the microscopic examination of cut, polished and etched sections.

Seventh, That when solid steel is partially decarburized by oxidizing agents, at between 700° and 800°, a ring or envelope of pure iron forms at the surface, and the granules in this layer assume a columnar structure radiating from the outside to a point below where there is carbon. The oxidizing agent almost certainly consists of carbonic acid largely diluted with carbonic oxide. The columnar granules assume the ordinary equi-axed form on heating to 900° C. and cooling quickly. On very slow cooling through 800° to 600° they re-form.

Eighth, That by strongly etching pure iron or iron containing much phosphorus, aluminium or silicon, square crys-

tals, apparently in the form of flat plates, are readily developed, confirming what is universally acknowledged, that iron crystallizes in the cubic system.

Ninth, That by mechanically testing microsections of pure iron by the method described in a previous paper, such of the grains as are built up of crystals with cleavages at right angles to the surface break up or fracture in two directions, one at right angles to the other, which not only tends to prove that the crystalline system is cubical, but shows that large crystalline granules in iron are a great source of weakness, and that probably the gradual development of fracture in steel shafting, etc., subjected to rough usage may be greatly due to the breaking up of the iron crystal masses themselves through the planes of cleavage weakness. In the trials made it was found that if the shock was not too violent the cracks terminated at the junctions of the grains. It would seem to follow, then, that the smaller and finer the the grain the safer the structure. This coincides with the researches of Brinell, Sauveur and others.

Tenth, That soft steel plates treated under certain conditions develop a most peculiar crystalline structure, in which the granules, although not larger than usual, are built up of crystals having their axes and cleavages in nearly the same phase throughout, and that as a consequence they are easily fractured in two main directions, one at right angles to the other, and that these cleavage lines are invariably at an angle of 45° to the direction in which the plates are rolled. This extraordinary development is sometimes, but not always, destroyed by close annealing for thirty-six and forty-eight hours, but it is invariably destroyed by heating to 900° C., and then becomes exceedingly tough.

Some of these specimens, after restoring in that way, on rerolling in the usual way had the rectangular weakness redeveloped, but in other trials rerolling did not cause redevelopment of the peculiarity.

The rectangularly brittle sheets were usually low in carbon, 0.03 to 0.06 per cent ; but many good sheets were also nearly as low, although they generally varied between 0.06 per cent and 0.09 per cent. The very thin sheets which never developed brittleness were very low in carbon, 0.03 to 0.05 per cent.

So far the attempt to reproduce at will the peculiar brittleness has not been completely successful, which shows clearly enough that we do not thoroughly know all the conditions under which it is developed.

In drawing this paper to a close, I must apologize for its length and its incompleteness; but if it has no other effect than that of proving how ignorant we are, and of stimulating others, especially the younger members of our Society, to prosecute original research, and endeavor to clear away the darkness and obscurity which surround so many processes, especially the heat treatment in the metallurgy of steel and iron, I shall be fully repaid.

Finally, I must acknowledge the value of the metallographic methods of investigation, so long neglected, which was originated more than thirty years ago by our esteemed countryman, Dr. Sorby of Sheffield. I must also acknowledge the valuable assistance in working out the foregoing results in this paper of quite an army of practical metallurgists, amongst whom I must specially mention Messrs. John Lysaght, Ltd., Wolverhampton, Mr. R. A. Hadfield, Mr. J. L. Potts, Messrs. J. H. Andrew & Co., Sheffield, Mr. W. H. Panton, Professor Roberts-Austen, Mr. T. Sorby, Mr. David Evans, Mr. F. Seaman, Messrs. the Wigan Coal and Iron Co., Ltd., Mr. W. H. Hewlett, Mr. E. H. Saniter, Mr. A. Cooper and Mr. C. H. Ridsale.

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ALLOYS.*

By Prof. CHANDLER ROBERTS-AUSTEN, C.B., D.C.L., F.R.S.

THE advance in our knowledge of alloys since the last course of Cantor lectures was delivered in 1893 has been noteworthy. It will be well to deal first with that portion of the subject which has already been partly treated in the foregoing lectures of the present course. The question of points of solidification of alloys must still, therefore, occupy our attention.

Rudberg was, I believe, the first to give measurements of the points of solidification of a series of associations of two metals which would enable a curve to be constructed; his work, however, only dealt with the easily fusible series of lead and tin alloys, the melting-points of which were well within the range of the ordinary mercurial thermometer.

The curve showing the points of solidification of the silver-copper series published twenty-three years ago by me in the *Proceedings of the Royal Society*,† was the first which represented what is now justly called the "freezing-point curve" of a series which is beyond the range of the glass thermometer, and therefore demanded pyrometric work. The method adopted was very imperfect, for it consisted in transferring a ball of iron from the just molten alloy to a calorimeter. The curve, however, plotted from the results of the experiments truly revealed the nature of the alloys under examination and, viewed in the light of modern knowledge, the curve shows to which group of solutions the copper-silver series belongs. At that time the melting-point of silver was taken to be 1040° C., while that of copper was unknown, but was believed to be much higher than subsequent experiments have proved it to be. Nevertheless, if the results given in

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that paper of over twenty years ago be corrected to bring them
into accordance with modern measurements of the freezing-
points of silver and of copper, it will be seen that the con-
cordance is somewhat remarkable. The more important part
of my old curve of 1874, corrected for the freezing-point of
silver which is now accepted, is therefore plotted in Fig. 1,

FIG. 1. SILVER-COPPER ALLOYS.

SILVER PER CENT.
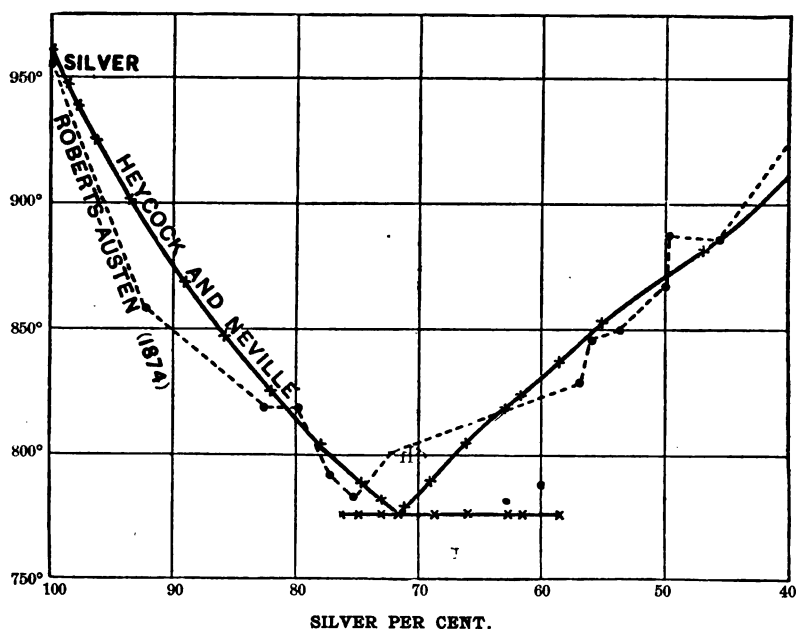
together with the results recently obtained by Heycock and
Neville,* whose very accurate determinations may be taken
to be final. In both sets of results percentages by weight of
the constituent metals are given, and not atomic percentages.
With reference to what is now called the *eutectic* alloy, that is
the most fusible alloy of the series, the following statement
was made by me in 1874 with reference to the alloys of silver
and copper: " I anticipated that Levol's homogeneous alloy,
which contains 718.93 parts of silver in 1000, would have the

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* *Phil. Trans. Royal Soc.*, Vol. CLXXXIX (1897), pages 25-70.

lowest melting-point," but the experimental results pointed to another alloy containing 630.3 of silver per thousand, as having a still lower melting-point. It is evident that this result was due to the imperfections of the method which did not enable the last point at which the alloy remained fluid to be determined accurately, and this early inaccuracy was corrected in 1891, when almost the first experiments made with the recording pyrometer were devoted to a re-examination of the copper-silver series.* I showed that Levol's alloy appears to be the only one with a single freezing-point, which points to its being the eutectic alloy of the series, but as there are theoretical reasons for considering that eutectics cannot be definite chemical compounds, and the composition of Levol's alloy corresponds accurately to the chemical formulæ, Ag_3Cu_2, I doubted whether it was really the eutectic alloy of the series, but any question as to whether Levol's alloy is the true eutectic of the silver-copper series has, since this lecture was delivered, been set at rest by M. Osmond,† who, by microscopic evidence, proved the alloy to have the banded "pearly" structure of a eutectic alloy; that is, it possesses exactly the structure which a solidified "mother liquor" should have. I am indebted to him for the accompanying photograph,‡ Fig. 2, of Levol's alloy which shows this beautiful pearly structure, and brings the eutectic of the silver-copper series into line with the "pearlyte" or striated portion of Fig. 7 of the last lecture, which represents the eutectic of the carbon-iron series of solutions.

I have dwelt on these historical facts at some length, because it was this old work, published by the Royal Society in 1874, which led my friend and colleague, Professor Guthrie, to examine the constitution of alloys in the course of a memorable research, which proved very fruitful in his skilful hands, as it enabled him to connect the *cryohydrates* of saline solutions with the *eutectics* in alloys. The whole question of the

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* First Report to the Alloys Research Committee. *Proc. Inst. Mech. Eng.*, October, 1891.

† *Comptes Rendus*, Vol. CXXIV (1897), page 1094.

‡ M. Osmond has since published this photograph in his admirable communication to the Association internationale pour l'essai des matériaux. Stockholm (1897). Also, *The Metallographist*, 1898, page 5. — ED.

fusibility of alloys has been studied by Professor H. Le Chatelier.* He points out that in considering alloys as solutions, it is necessary to modify the view in which ordinary solutions are regarded. In ordinary chemical language, it is usual to distinguish the solvent from the body which is dissolved, but really the two bodies play the same part. Many aqueous solutions, as he shows, can exist below the freezing-point of water — that of chloride of calcium, for instance, which is

FIG. 2.

liquid down to $-55°$ C. He demonstrates that the typical curves which represent the fusibility of alloys have in each case corresponding curves of saline solutions, and he quotes experiments by Lœwel, Bakhuis Roozeboom, together with his own results, in confirmation of the facts. He specially refers to the curves of fusibility of isomorphous mixtures of certain organic substances first recorded by Kuster.† The

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* Professor Le Chatelier's more important memoirs on this subject are the following :

Comptes Rendus, 1894, Vol. CXVIII, pages 350, 415, 638, 709 ; 1895, Vol. CXX, pages 835, 1050.

Bull. de la Soc. d'Enc., May, 1895, page 569.

"Recherches sur la Dissolution." *Annales des Mines,* February, 1897.

† *Zeitschrift für Phys. Chem.,* Vol. VIII, page 577.

result of Le Chatelier's very interesting work is the division of the curves of alloys into the following classes :

In the first of these, *the metals dissolving each other give neither definite compounds nor isomorphous mixtures.* The curves of this class consist of two branches as is shown by the lead-tin curve in Fig. 3 [and Fig. 5 of Lecture I],* in which com-
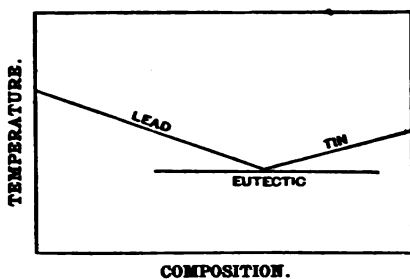
FIG. 3.

position and temperature are co-ordinates, and it would appear that when a curve is composed of two branches only it is safe to conclude that after solidification the two isolated metals are simply in juxtaposition. In the second case, *the two metals give rise to one or more definite compounds.* Now as in the case of a solution of sulphate of soda in water one branch of the curve is peculiar and characteristic. If the compound which is formed between the two metals fuses without dissociation, there will be a maximum-point in the curve which corresponds to the definite compound. In this case the curve will be of the form shown by the gold-aluminium curve, Fig. 4.

I had the good fortune to be the first to show † that such a curve could exist in the case of the metallic alloys with the point of minimum fusibility higher than that of the
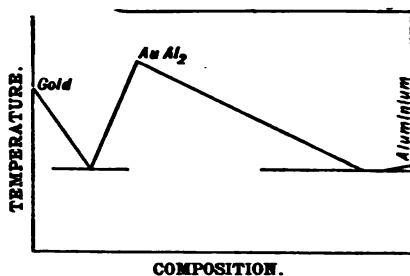
FIG. 4.

least fusible constituent, for the gold-aluminium curve was exhibited at a lecture delivered at the Royal Institution, on February 5, 1892. M. LeVerrier has shown that a similar curve may be traced for the aluminium-copper series, and H.

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* *The Metallographist,* April, 1898. — ED.
† *Proc. Royal Inst.,* 1892.

Le Chatelier * has found similar curves for the copper-tin. The copper-tin series has been very fully worked out by Mr. Stansfield in my laboratory.† In the case of my own curve of the aluminium-gold series the maximum-point occurs, as Fig. 4 shows, at the alloy $AuAl_2$, the freezing-point of which is no less than 35° higher than that of gold itself. If the compound formed in the alloy is dissociated, the portion of the curve which marks its presence will be rounded.

In the third case *the two metals which are dissolved in each other form isomorphous mixtures.* In this group the freezing-points of the alloys of the series lie on a straight line, Fig. 5, and so far as I am aware the silver-gold alloys examined by Schertel ‡ presented the first known case. This question is very important, and I long ago suggested it as a subject for investigation to my colleague, Dr. Rose, who is now engaged upon it. M. Gautier has recently given several instances of such isomorphous alloys,§ and among them the antimony-bismuth and the silver-zinc may be cited.
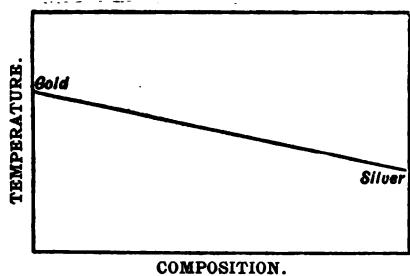
FIG. 5.

It will be remembered that in the curves to which reference has just been made, there are in addition to the *initial* freezing-points of the respective members of each series of alloys, freezing-points of the various *eutectic* alloys of each series, represented by horizontal lines, there being usually, as has already been stated, only one alloy in each series in which the initial and the final freezing-points coincide, and are blended in a single point. The study of these *eutectic* alloys in the case of metals with melting-points beyond the range of the ordinary mercurial thermometer was begun, so far as I know, in the experiments with which I was entrusted

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* *Bull. de la Soc. d'Enc.,* May, 1895.
† *Proc. Inst. Mech. Engineers,* 1897.
‡ *Poggendorf Annalen,* 1897, page 368.
§ *Bull. de la Soc. d'Enc.,* Vol. I (1896), page 1293.

by the Institution of Mechanical Engineers,* and the subject
has been very fully developed in the Fourth Report commu-
nicated to the Institution at the end of 1896. Messrs. Hey-
cock and Neville also record the presence of eutectics in the
very valuable series of "complete freezing-point curves"
which have recently been published by the Royal Society.†
The pyrometric method they adopted does not in all respects
appear to be well adapted for the detection of the presence of
small quantities of eutectic alloys, and their work needs some
amplification in this respect; but they have given us by far
the best series of initial freezing-points we as yet possess.

The liquidation of impurities in metallic copper formed
the subject of an interesting paper by Mr. E. Keller, ‡ who
shows that when plates or ingots of copper solidify, the im-
purities are driven to the "center of solidification," that is to
the portion of the mass which solidifies last. They follow
the order of their atomic volumes, and he states that the order
of segregation in the case of the impurities in copper, in the
main, corresponds with that in lead bullion recorded by Scher-
tel.§ Since the lecture was delivered an interesting paper
showing the distribution of gold and silver in lead has been
published by Mr. Arthur Claudet.‖

Turning to quite another subject, M. J. B. Senderens ¶
has made a very interesting series of experiments on the pre-
cipitation of one metal from solution by another metal. He
points out that Richter in his researches, published between
the years 1796–9, was led to the promulgation of a law which
is now expressed as follows: " Metals are precipitated from
their saline solutions atom for atom of the same valency."
Senderens shows that this is not rigorously accurate, as the
amount of the precipitating metal is always in excess. For
instance, take the well-known reaction employed in refineries

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* *Proc. Inst. Mech. Eng.* Minutes of Proceedings, February 4, 1897.

† *Phil. Trans., loc. cit.,* and *Trans. Chem. Soc.* (1897), page 383.

‡ *Trans. American Institute Mining Engineers.* Chicago meeting,
February, 1897.

§ Quoted by Hofman. *Metallurgy of Lead,* page 244.

‖ *Trans. Institution of Mining and Metallurgy,* 1897.

¶ Senderens. *Bull. Chem. Soc. Paris,* Vol. XV (1896), pages 208,
691 ; and Vol. XVII (1897), page 271.

for the precipitation by copper of silver from its solution as sulphate, in accordance with the equation :

$$Ag_2So_4 + Cu = Ag_2 + CuSo_4.$$
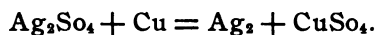
If a solution of sulphate of silver containing 4–5 grammes of the salt in the liter of water be employed, it will be found that after a plate of copper has been immersed in the solution for seven days, that it will have lost 0.012 gramme more than theory demands. Senderens shows that this fact is of singular interest in relation to the allotropy of iron, but his work is quoted here on account of its bearing on the formation of alloys in the " wet way." He points out that several chemists have thought that alloys might be so prepared, and that among them Planche and Brugnatelli [*] may be specially mentioned, and that Gay-Lussac [†] at first favored the opinion, but abandoned it later. [‡]

The history of this subject is very interesting. So long ago as 1857, Odling [§] published a paper on " The Reciprocal Precipitation of the Metals," the outcome of a paper he had communicated to the Cheltenham meeting of the British Association in 1856. The paper is a very remarkable one, for Odling shows that in one experiment only 0.72 of an equivalent of cadmium precipitated an equivalent of copper from its solution of neutral chloride. He also pointed out that conversely, if clean copper foil be placed in chloride of cadmium, it will precipitate cadmium on the foil, and he found, moreover, as he says, "that a piece of copper coated with cadmium and a coil of copper and cadmium foils rolled up together behave very differently when treated with hydrochloric acid . . . the metallic deposit of cadmium partakes of the character of an alloy," and he attributes this precipitation of one metal on another "to the affinity of one metal for the other." In other words, he formed alloys in the wet way.

More recently Mylius and Fromm [‖] have shown that alloys may be precipitated from dilute solutions by zinc, cad-

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[*] *Journ. de Phys. et de Chem.*, Vol. III, page 426.
[†] *Ann. de Chim.*, Vol. LXXIX, page 91.
[‡] *Ann. de Chim. et de Phys.*, Vol. VII, page 219.
[§] *Chem. Soc. Journ.*, Vol. IX (1857), page 289.
[‖] *Ber. d. d. Chem. Ges.*, Vol. XXVII (1894), page 630.

mium, tin, lead and copper. Thus a strip of zinc plunged in a solution of sulphate of silver, containing not more than 0.03 grammes of silver in the liter, becomes covered with a flocculent precipitate which is a true alloy of silver and zinc. In the same way when copper is precipitated from its sulphate by zinc the alloy formed is brass. They have also formed certain alloys of definite composition such as $AuCd_3$, Cu_2Cd, and more interesting still, Cu_3Sn. I have elsewhere pointed to the interest these experiments possess in relation to the diffusion of solid metals,* and I may add that many years ago I showed that the interpenetration of iron and copper will take place, during the electro-deposition of copper, even through a thin electro deposited film of nickel on the copper.

Senderens points out that alloys will probably be produced in even more concentrated solutions than those employed by Mylius and Fromm, and he reminds us that Gay-Lussac showed that in the reduction of a solution of nitrate of silver by copper, the first portions of silver deposited are usually pure.

It is singular that when lead is reduced from its acetate by zinc the reduced lead appears to be pure, and it is well to remember that lead reduced from its sulphate by zinc (Bolley) has been claimed as an allotropic variety of the metal.

Among the more recent developments of our knowledge of alloys are the experiments by Heycock and Neville on the alloys of sodium and gold. They find that when sodium dissolves gold, if the resulting alloy is treated with alcohol and finally with water, a beautifully crystalline mass is left consisting of lustrous needles.† They are of a full brassy color, but if they are heated to about 200° C. they become incandescent, and their color changes to that of pure red-gold. After ignition, but not before, the residual sodium can be extracted with water and estimated. The percentage of sodium agrees pretty well with the formula Au_3Na.

In a very interesting lecture delivered April 2, 1897, at the Royal Institution, Heycock showed that by the aid of the X-rays the crystals of opaque gold might be seen in the

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* Bakerian lecture. (1896.)

† *Science Progress*, Vol. IV (1895), page 183.

sodium which is transparent to the X-rays, and in this way
liquation in the sodium-gold series may be studied during
solidification.

One other question of much interest is being investigated
by Heycock and Neville.* It is connected with the curious
behavior of the zinc-silver series of alloys. Percy,† in ex-
amining this series, called attention to the fact that an alloy
containing 49.72 per cent of silver and 50.28 zinc, has a sur-
face which was "copper-red immediately after solidification."
"The color of its fracture when broken cold was white and
very bright, but when broken hot the fracture immediately
acquired a yellow, red, purple or blue tarnish according to
the temperature." Dr. Percy's collection, now at the Royal
School of Mines, contains the specimens he prepared, and the
fractured fragments vary from golden yellow to blue. The
great interest of Heycock and Neville's work is derived from
the fact of their showing that the color is not, as Percy
thought, due to tarnish, for they find that the color may be
produced by heating the alloy to 150° in *vacuo*, and cooling it
quickly. If the alloy be placed on an iron plate, heated by
a gas flame from below, and if it be then quenched in water,
the red color will appear. It seems to me that this is due to
an allotropic change analogous to that already described in
the case of the lead, bismuth-tin alloy‡ known as Newton's
metal, more especially as the change of the normal modifica-
tion to the red may certainly be produced by longitudinal
stress under circumstances in which the alloy does not become
heated. It is interesting to remember also in connection with
the allotropy of this alloy, that zinc has a critical point at 150°.

With reference to the colored alloys, Gautier has recently
pointed out§ that certain members of the silver-cadmium
series are violet, and suggest the well-known violet alloy of
copper and antimony, but in its case one of these metals, the
copper, is a colored one. It is strange that the union of
metals with such faint coloring as silver, zinc and cadmium

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* *Proc. Phil. Soc. Camb.*, Vol. IX, Part IV.
† *Metallurgy of Silver and Gold*, 1880, page 170.
‡ Second Report to the Alloys Research Committee, page 127.
§ *loc. cit.*

should produce a mass which is capable, under suitable thermal treatment, of becoming highly colored.

It is really remarkable how much has of late years been done in elucidating the nature of alloys, but much remains to be done. Guthrie's great generalization respecting the constitution of eutectic alloys has been most fruitful, and it seems certain that they at least are not chemical compounds. Eutectics always appear to solidify with a fine-grained structure like the pearlyte of the carbon-iron series, and in eutectic alloys we shall probably find that movements in the *solid* are most pronounced and interesting. With reference to the influence of valency in alloys, Neville has made the following very suggestive observation.* He says: "Dr. Foerster† suggests that alloys of definite composition, such as AuCd, Cu₃Sn and others, many of which do not obey the ordinary laws of valency may be held together rather after the fashion of double salts; may, in fact, be *molecular* and not atomic compounds. In this case they may be dissociated when in solution, but, like the alums, exist in the solid form." He forcibly adds: "It is certainly somewhat difficult to imagine that the electropositive and self-saturating atoms of gold and cadmium can be held together in the molecule AuCd by forces similar to those which maintain the equilibrium of a molecule of hydrochloric acid."

The remarkable property which some alloys of nickel and iron possess of having a coefficient of expansion nearly equal to zero suggested the desirability of employing these alloys for the construction of measuring instruments. With this object in view M. Guillaume ‡ has determined the densities and modulus of elasticity of a series of alloys of iron with 4 to 45 per cent of nickel. One curious result in the case of alloys with 25 per cent of nickel is that a rule made of this alloy and annealed at a given temperature continues to elongate when it is kept at a lower temperature. He also finds that an alloy containing 22 per cent of nickel expands when it is heated considerably more than ordinary steel does, but

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* *Science Progress*, Vol. IV (1895), page 187.

† *Naturwissenschaftliche Rundschau*, 1895.

‡ *Comptes Rendus*, Vol. CXXIV (1897), page 176, and *ibid.*, page 752 and page 1515; also Vol. CXXV (1897), page 235.

an alloy of iron with 37 per cent of nickel hardly expands at all, so that the presence of an additional 15 per cent of nickel in nickel-iron alloys is sufficient to entirely change the nature of the metal.

The most recent work on the microscopic examination of alloys is that of M. Charpy,* who has arrived at the following conclusions. The microscopic examination of metals renders it possible to obtain indications as to the nature of the work to which the sample has been subjected. It furnishes also important information as to the chemical constitution of alloys. It affords in some measure a rapid analysis of metallic alloys. It renders it possible to establish the fact that the solidification of alloys is effected in the same way as in the case, which is easier to observe directly, of the solidification of saline solutions, and that binary alloys are usually formed of two constituents only, whatever may be the number of definite compounds formed by the two allied metals.

The type of the normal constitution presents, therefore, crystals of a simple metal or of a definite compound, surrounded by a second constituent, which is usually a eutectic mixture, which is itself formed of two finely divided elements, of which one is that which forms the crystals. The composition of the eutectic mixture remains constant, the proportion of the isolated crystals varies with the percentage composition of the alloy.

Beyond this normal type, in which it is necessary to include the limiting cases which correspond respectively to a pure definite compound, or to a pure eutectic mixture, there is only a second type, that of metals which give isomorphous mixtures. These alloys then are formed, whatever may be their composition, of a single kind of crystal occupying the whole mass; usually, the composition and the properties vary continuously in each crystal. Although there are a small number of metals which can form isomorphous mixtures, it seems that there are many cases of definite compounds of two metals which are isomorphous with one or

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* *Bull. de la Soc. d'Enc.*, Vol. II (1897), page 384. Also *The Metallographist*, April and July, 1898. — ED.

other of them.   Microscopic examination leads, for instance, to the prediction of a compound of tin and antimony containing about 50 per cent of tin and isomorphous with antimony.

There also appears to be a compound of antimony and silver containing about 20 per cent of antimony and isomorphous with silver ; a compound of tin and silver containing 30 per cent which is isomorphous with silver.   These are, however, only indications which demand confirmation in the attempt to isolate these compounds.

The constituents of metallic alloys usually fall out in the form of *crystallites* and not as well-defined crystals.   The form of these constituents is usually only approximately indicated. But apart from this character it is possible to recognize these constituents by their color, their hardness, and especially by the way in which they behave in relation to various re-agents.

The method of preparation, and especially the degree of rapidity of solidification, modifies considerably the dimension of the *crystallites*, but it does not seem to exert any other influence on the constitution of the alloy.

Among the numerous experimenters who are now studying the constitution of alloys by micrometallography, Mr. Stead is taking a very high place.   He has sent me some admirable microphotographs of the tin-antimony-copper alloys, and of many others.

Not the least singular of recent observations is one which will be found in a paper by M. Osmond and myself.*   Osmond finds that a cast mass of gold alloyed with $\frac{2}{10}$ per cent of antimony shows, when etched with sulphuric acid, a large crystalline structure, but if it be annealed at a temperature of only 200°, the original structure disappears, and etching with sulphuric acid then reveals a fine-grained structure resembling hardened steel.   This transformation of the structure of a metal at a temperature so far below its melting-point, in the presence of only $\frac{2}{10}$ per cent of a foreign body, appears to open up a new field for research.

I wish that space permitted me to deal with the curious problems involved in the constitution of such alloys as manganin, platinoid and other alloys of this class ; these must,

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* *Phil. Trans. Roy. Soc.*, Vol. CLXXXVII (1896), page 430.

however, be left for a future occasion. I will content myself with pointing out, in conclusion, that the tendency of modern research in connection with alloys is towards the study of molecular movement in solid masses, and to what is called the atomic grouping or "chemistry in space" of the allied atoms.

The Microstructure of Iron and Steel. — In a paper presented to the June, 1898, meeting of the American Foundrymen's Association, Mr. S. S. Knight calls attention to the limitation of chemical analysis due to the impossibility of detecting by chemical tests changes of heat treatments which may nevertheless so deeply alter the physical properties of metals.

Mr. Osmond's paper on Microscopic Metallography [*] is reviewed in part and his illustrations reproduced.

The author, endorsing Prof. Arnold's theory, attributes the hardening of steel to the retention by sudden cooling of a hard sub-carbide of iron, answering to the formula $Fe_{24}C$.

These subjects have been exhaustively discussed elsewhere in *The Metallographist.*

Attention is called to the wide field opened to the science of metallography and to the benefits which might be derived from the use of the microscope in foundry works.

Bibliography of the Metallography of Iron and Steel. — The following memoirs by Prof. D. Chernoff should be added to Mr. Colby's bibliography published in the April, 1898, number of *The Metallographist* (Vol. I, page 168).

Professor Chernoff's masterly researches have long ago become classical, and should be carefully studied by every student of the metallurgy of iron and steel.

Their chronological position in Mr. Colby's list is readily indicated by the accompanying numbers.

4a. D. CHERNOFF — Remarks on the Manufacture of Steel and the Mode of Working it. Communicated to the Imperial Russian Technical Society in April and May, 1868. — Translated into English. London, William Clowes & Sons.

4b. —— Structure of Cast-Steel Ingots. Communicated to the Imperial Technical Society, Dec. 2, 1878. — Translated into French, Revue Universelle des Mines, 2d series, vol. vii, 1880, page 140. — Translated into English, Proc. Inst. of Mech. Eng., January, 1880.

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[*] *Trans. Am. Inst. of Mining Engineers*, Vol. XII, 1893, page 243.

CORRESPONDENCE.

The Segregation of Cementite.

To the Editor of *The Metallographist.*

Sir : — You ask whether the branch EN which, in my reply to your paper " The Microstructure of Steel and the Current Theories of Hardening " (Fig. 4, page 9, of the author's edition),* representing the segregation of cementite in hypereutectic steels (i. e., containing more than 0.9 per cent carbon), corresponds to some evolutions of heat experimentally ascertained ?

As a matter of fact, the existence of this branch EN is indicated at the same time,

A, by the study of the microstructure;

B, by certain cooling curves.

I shall examine separately the proofs furnished by each of these two methods.

A. 1°. If a steel containing about 1.50 per cent of carbon is hardened as intensely as possible, by quenching it in a mixture of ice and water, for instance, the results vary considerably with the quenching temperature. If this temperature is equal to 1100° C. or higher, the quenched metal contains only traces of cementite; if quenched at 800° C., the cementite is abundant: the carbide Fe_3C, therefore, began to segregate at an intermediate temperature.

2°. Let us take a bar of the same steel and heat one of its extremities to 1100° C., while the other remains below a dark red; let us quench the bar, as previously, in ice water, and let us examine the microstructure of a longitudinal section. The cementite is absent (or nearly so) at the extremity which was most heated; it begins to appear at a certain point corresponding to a certain quenching temperature, and then increases progressively until the normal proportion is reached; finally pearlyte takes the place of martensite in the region where the temperature had not reached that of the triple point of transformation.

These experiments are conclusive, and from them I have learned the existence of the branch EN of my diagram.

B. Now, is the segregation of free cementite a cause of evolution of heat?

Yes, evidently, since it is a phenomenon of solidification.

But will this heat be visible on the cooling curves?

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* See Fig. 3, page 220, of *The Metallographist* for July, 1898. — ED.

We cannot assert it, *a priori*, for if the segregation of cementite is progressive, there will not be any *sudden* liberation of heat, therefore no critical point, but only a slight rising of the curve which will remain unnoticed. In order to produce a critical point a *notable* quantity of cementite must segregate *at the same time;* in other words, the segregation must begin in a *supersaturated* solution.

Is this condition fulfilled? We must ascertain it by experiments.

In the sample of steel containing 1.24 per cent of carbon which I used in my first experiments, I did not, *generally*, notice any critical point above Ar_{321}, but I did notice such a point *exceptionally*. This exceptional curve is precisely the one which I published in 1890 (*Journal of the Iron and Steel Institute*, Part I, Plate III; hard steel). The liberation of heat is very marked between 870° and 830° C., only I did not then understand its meaning.

Professor Roberts-Austen has found more recently corresponding evolutions of heat in steels containing, respectively about 1.60, 1.80 and 1.90 per cent of carbon, and it happens that Professor Roberts-Austen's points and my own group themselves satisfactorily around a line which passes by the point of intersection of the two other branches already known ("Cantor Lectures on Alloys," March 22 and 29, Fig. 9).*

It follows from these facts that the beginning of the segregation of cementite *may* be indicated by a critical point, but that it is not necessarily so, because the supersaturation upon which this point depends is by nature a somewhat capricious phenomenon. Metallography has in this connection lent us, once more, a useful assistance.

I shall add that the experiments which have been carried on are not sufficiently numerous to establish with great precision the shape and the exact position of the branch of curve which we are considering. But that this branch should be somewhat inclined to the right or to the left, should be straight or curved, matters little; the essential point is that the case of steel has been made to fall into line with the general theory of liquid solution.

F. OSMOND.

PARIS, May 12, 1898.

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* See Fig. 1, page 343, of the present number of *The Metallographist*. —ED.

The Allotropic Theory and the Hardening Power
of Low-carbon Steel.

To the Editor of *The Metallographist.*

Sir: — In your July issue on page 268 Mr. Osmond states
that the results published by Professor Howe in the *Journal
of the Iron and Steel Institute* were confirmed by me in a com-
munication made to *Engineering* in July, 1897. This state-
ment is not accurate. My experiments were made on nearly
pure iron, and the maximum stress observed was about 33 tons
per square inch. Professor Howe's results were obtained by
quenching impure mild steel, and his maximum stress was
about 100 tons per square inch. The whole diminution of
tenacity noted by me was not more than one of the errors of
experiment detected on plotting Professor Howe's figures.
The critical point Ar_1 was not visible in my recalescence
curve, and allowing for small errors of experiment, my tenac-
ity curve showed that the diminution in tenacity was roughly
proportional to the quenching temperature between the tem-
peratures of 450° and 920° C. I also proved that the ductility
as measured by the percentage of reduction of area was con-
stant (at about 80 per cent) for the whole range of temperature
between 15° and 920° C. All this I some time ago pointed out
in *Engineering* in reply to Professor Howe's criticism of my
communication, but this Mr. Osmond has seen fit to ignore
and make a statement which, to put it mildly, is misleading.
I, in common with most steel metallurgists, am quite unable
to follow Mr. Osmond's meaning when he compares and,
indeed, ascribes to a common cause the trifling hardness
produced on quenching iron with the adamantine hardness
produced by quenching steel. Quenched iron is quite soft,
quenched steel is flint-hard. The reduction of area of quenched
steel is *nil*, that of quenched iron about 85 per cent.

Again, how can an increase in tenacity almost equally
distributed over a range of 400° C. mechanically prove allot-
ropy at two thermal points, one included in a range of about
15°, and the other extending over about 30° of temperature?

The two points may exert some little influence (not neces-
sarily due to allotropy at all), but such is hardly capable of

separate mechanical measurement. There seems little doubt that the main factor determining the stiffening of quenched iron is something (probably stress) quite unconnected with the critical points, inasmuch as the development of rigidity can be detected at least 200° C. below even the position of Ar_1, which point, as I have said, could not be recognized in my experiments.

Turning to another matter I note also that Professor Roberts-Austen states that Dr. Hicks and Mr. O'Shea have confirmed his recalescence results on electrolytic iron. This statement is hardly in accordance with fact. Professor Roberts-Austen is well aware that the results he quotes were obtained by me, as my friends have not yet made their thermal observations, which will be determined by an energy method. Moreover, my results are not altogether in accordance with those of Professor Roberts-Austen. He found that the point Ar_3 was truly reversible, I, that it appeared about 20° C. higher during heating than cooling. He also said that the point Ar_2 was so faint as to be barely visible on the curve, a statement which has recently led Mr. Saniter into a grave error. I find Ar_2 to be distinctly visible in pure electrolytic iron. Professor Roberts-Austen found electrolytic iron to be flint-hard. The iron prepared by Dr. Hicks and Mr. O'Shea was brittle, but quite soft. Yours faithfully,

J. O. ARNOLD.

UNIVERSITY COLLEGE, SHEFFIELD,
July 16, 1898.

Professor Arnold refers in the above letter to an article published in *Engineering* of July 9th, 1897, in which he describes some experiments undertaken for the purpose of ascertaining the influence of sudden cooling upon nearly pure iron. His conclusions were that the "critical thermal points Ar_2 and Ar_3 are as such without influence on the mechanical properties," that "between 500° and 900° C. the increase of tenacity is proportional to the quenching temperature," that, "in his opinion, the increasing tenacity, as the temperature of quenching rises, is the measure of crystalline stresses, internal and external."

Professor Arnold's conclusions were opposed by Professor Howe in an article published in *The Engineering and Mining Journal* of September 25th, 1897, and by Mr. Sauveur in a communication to the same journal of October 23d. Both writers endeavored to show that Professor Arnold's results, instead of supporting his propositions, clearly indicated the influence of the critical points upon the hardening power of his low-carbon steel, — that the increase of tenacity, far from being proportional to the quenching temperature, exhibited three marked and sudden elevations corresponding closely to the thermal critical points, and which could not be attributed, as he suggested, to experimental errors.

Professor Arnold replied to Mr. Howe's criticisms in a note published in *Engineering* of October 22d, in which he insists on the accuracy of his position.

In the present communication Professor Arnold, while again reasserting the truth of his conclusions, fails to mention, thus peremptorily setting aside, the objections which they had called forth.

It was, therefore, necessary to fill this omission in order that the impartial student (and can there be any others?) might acquaint himself with the whole of the controversy before passing judgment on the point at issue. — ED.

INDEX.

[The names of authors are printed in SMALL CAPITALS and the titles of articles in *italics*.]